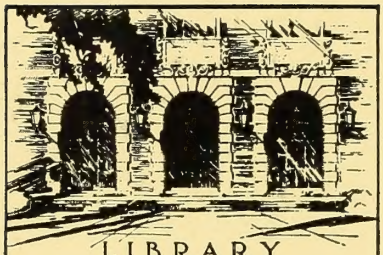


[redacted]

I N O R G A N I C S E M I N A R

1944-1945

TABLE OF CONTENTS

TABLE OF CONTENTS

Table of Contents (continued)

Table of Contents (continued)

THE COORDINATION NUMBER OF COPPER IN THE POLYETHYLENE-AMMONIUM CHLOROCUPROATES

Hans Jonassen October 24, 1944

Coordination numbers from one to six have been reported for the coordination of chloride ions to the central copper ion in the presence of excess chloride ions.

In the study of absorption spectra of copper chloride solutions, Getman (1) reported in 1922 that in solutions containing copper and chloride ions the displacement of the region of maximum transmittency toward longer wave-length with increasing chloride ion concentration was due to the displacement of the equilibrium:

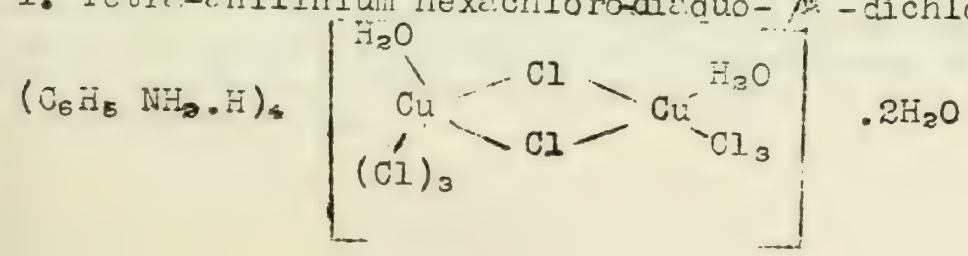
$$Cu(H_2O)_4^{+2} + 4Cl^- \Longleftrightarrow CuCl_4^{-2} + 4H_2O$$

Spacu and Murgulescu (2) reached similar conclusions from spectrophotometric studies of the system. They postulated the formation of both $CuCl_4^=$ and $CuCl_3^-$ complexes in such solutions. Babko(3) obtained data which indicated the presence of the following chlorocuproates in such solutions: $CuCl^+$, $CuCl_3^-$, $CuCl_4^=$. Bhagwat (4) ascribed the inapplicability of Beer's Law to copper chloride solutions to the presence of such complex ions as $CuCl^+$, $CuCl_3^-$, $CuCl_4^=$, as well as the Cu^{+2} ion itself. Moeller (5), applying a modification of Job's method of continuous variation to a solution of copper containing excess chloride ions, obtained data which seemed to prove definitely the presence of $CuCl_4^=$ ions in the solution, but his data do not preclude the existence of any other chlorocuproates. All the data cited above seem to indicate that the colors of the $CuCl_4^=$ and $CuCl_3^-$ are yellow rather than blue.

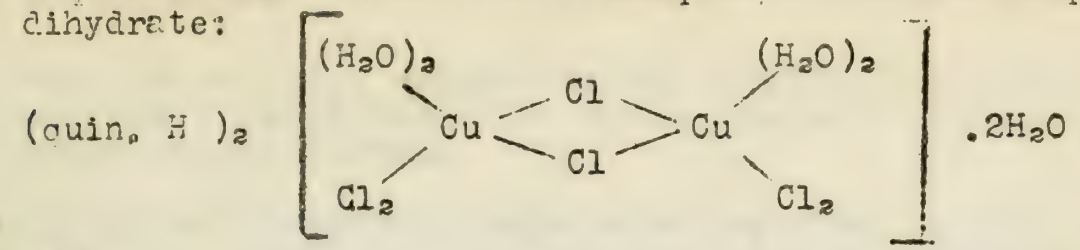
Similar complexes also have been prepared in the crystalline state. Topsoe (7) reported the preparation of yellow chlorocuproates of methylamine, dimethylamine and trimethylamine. In 1906, Grossman and Schuack (8) prepared the tetrachlorocuproate of ethylenediamine. The series of chlorocuproates of organic substitued monoamines was extended by Remy and Laves (9), Dehn (10), Michaelenko (11), and Amiel (12, 13). The chlorocuproates isolated by these authors contained $CuCl_3^-$, $CuCl_4^=$ complexes. The structures assigned to these indicated mononuclear complex ions, giving copper and coordination numbers of three, four, and five respectively.

In 1936 Dubsky and Wagenhofer (14) postulated a new theory. They maintained that all chlorocuproates prepared up to that time were really hexachlorocuproates of polynuclear structure containing two or more chloride bridges. They prepared a series of hexachlorocuproates to substantiate their theory. Two of the compounds prepared by them with the structures which they postulated are given below.

1. Tetra-anilinium hexachloro-diaquo-μ-dichlorodicopper dihydrate



2. Diquinolinium tetrachlorotetraaquo-μ-dichlorodicopper dihydrate:



Experimental

The research project started as an investigation of the complexes formed between copper and the straight chain polyethylene bases of the Hofmann series: diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. The complexes formed between an aqueous solution of copper sulfate and the amines could not be precipitated by the addition of an organic solvent nor by evaporation. Similar results were obtained with aqueous solutions of copper chloride; but when $CuCl_2 \cdot 2H_2O$ was dissolved in methanol and the amine was added to this solution a precipitate was formed. The first precipitate formed had a yellow color, but upon stirring and further addition of amine the solution solidified forming a green meal. After filtering, the green meal showed the presence of several solid phases: a yellowish green phase, a deep green phase, and a deep blue phase on the top layer. The blue phase of the top layer seemed to be a hydration product of the other two phases. Excess amine was added to part of the precipitate and it dissolved forming a deep blue solution. Concentrated hydrochloric acid was added to the remainder and a yellow precipitate was formed which was very soluble in water but which could be reprecipitated by the addition of an equal amount of concentrated hydrochloric acid. All the polyethylene amines gave similar yellow precipitates when prepared in a similar fashion.

Analysis showed that the following empirical formulae could be assigned to the compounds:

1. The diethylenetriamine complex: $NH_2C_2H_4NHC_2H_4NH_2.3HCl.CuCl_2$
2. The triethylenetetramine complex: $NH_2C_2H_4NHC_2H_4NHC_2H_4NH_2.4HCl.CuCl_2$
3. No reasonable empirical formula could be calculated for the tetraethylenepentamine complex with copper ion.

The first member of this series, the ethylenediamine complex, which had been obtained previously by Grossman and Schueck (8), was also prepared in order to compare its physical and chemical properties with those of the higher members of this series. Analysis showed it to have the following composition: $NH_2C_2H_4NH_2.2HCl.CuCl_2$

Discussion of Results:

Microscopic investigation showed that the en(ethylenediamine), dien(diethylenetriamine), and the trien(triethylenetetramine) complexes were translucent, showed birefringency, and had well defined crystalline configurations; whereas the tetren(tetraethylenepentamine) complex formed ill-defined opaque crystal clusters with only slight birefringency on the corners of the crystals. Molecular weight determinations by freezing point lowering showed that the complexes dissociated completely in aqueous solutions. This total dissociation was further substantiated by the following facts:

1. All the chloride present in the complex precipitated immediately, and only a short digestion was necessary to coagulate the silver chloride precipitate.

2. It proved possible to determine the total acidity of the aqueous solution of the complex by titration with sodium hydroxide. This would seem possible, only if the amine hydrochloride existed as such in the solution.

3. The blue color of the aqueous solution of the complex agreed both in color and in hue with an aqueous solution of copper ions of equivalent concentration.

4. Magnetic susceptibility measurements made by Amiel (15) on similar chlorocuprates showed that even in the solid state the magnetic properties of the copper in chlorocuprates are the same as those of the hydrated copper ion.

All of these facts seem then to point to the following conclusions:

1. The complexes dissociate completely in aqueous solutions.
2. Complete dissociation can only be explained if it is assumed that the complexes in the solid phase are linked by ion-dipole attraction.
3. With ion-dipole attraction only mononuclear chloro complex configurations would seem reasonable.
4. With mononuclear configuration the central copper ion seems to have a coordination number of four for the ethylenediammonium tetrachlorocuprate, of five for the diethylenetriammonium pentachlorocuprate, and of six for triethylenetetrammonium hexachlorocuprate.
5. Since these complexes dissociate completely in aqueous solution they can be said to exist as such only in the solid state; and in the solid state are obtained most easily in the presence of a high concentration of hydrochloric acid.

From these conclusions, the following structures have been tentatively assigned to these complexes.

1. En complex: $en.H_2$ $\left[\begin{matrix} Cl & & Cl \\ & Cu & \\ Cl & & Cl \end{matrix}\right]$

2. Dien complex: $dien.H_3$ $\left[\begin{matrix} Cl & & Cl \\ Cl & Cu & \\ Cl & & Cl \end{matrix}\right]$

3. Trien complex: $trien.H_4$ $\left[\begin{matrix} Cl & & Cl \\ Cl & Cu & Cl \\ Cl & & Cl \end{matrix}\right]$

BIBLIOGRAPHY

(1) Getman; J. Phys. Chem. 26, 217-246 (1922)

(2) Spacu and Murgulescu; Zeit. Phys. Chem. A 170, 70-80 (1934)

(3) Babko; Univ. etat de Kiev, Bull. Sci., Rec. chim. 4, 81-100, (1939)

(4) Bhagwat; J. Ind. Chem. Soc., 17, 53-59, (1940)

(5) Moeller; J. Phys. Chem., 48, 111-119, (1944)

(6) Job; Ann. chim., 10, 9, 113-203, (1928)

(7) Topsoe; Dansk Videns., 17, (1882)

(8) Grossman and Schueck; Zeit. anorg. Chem., 50, 1-20, (1906)

(9) Remy and Laves; Ber., 66B, 401-407, (1933)

(10) Dehn; J. Am. Chem. Soc., 48, 275-277, (1926)

(11) Michaelenko; J. Russ. Phys. Chem. Soc., 61, 2253-2267, (1929)

(12) Amiel; Compt. rend., 201, 964-966, (1935)

(13) Amiel; Compt. rend., 201, 1383-1385, (1935)

(14) Dubsky and Wagenhofer; Z. anorg. allg. Chem., 230, 112-122, (1937)

(15) Amiel; Compt. rend., 208, 1113-1115, (1938)

ROLL CALL

October 24, 1944

Ionization in Methanol — W. E. Morrell

By colorimetric (indicator) and conductimetric methods, Guss and Kolthoff (J.A.C.S., 66, 1484-88 (1944)) studied the behavior of SO_2 in methanol. They conclude that $CH_3-O-\underset{\underset{O}{\|}}{S}-O-H$ (cf. $H-O-\underset{\underset{O}{\|}}{S}-O-H$) is formed, and that its dissociation constant in methanol is 3×10^{-7}.

$$CH_3OH + SO_2 = CH_3OSO_2H = CH_3OSO_2^- + CH_3OH_2^+$$

$$\frac{{}^{a}CH_3OSO_2^- \cdot {}^{a}CH_3OH_2^+}{{}^{a}SO_2} = K_A = 3 \times 10^{-7}$$

(The constant for the corresponding dissociation in water is 2×10^{-2}.)

The authors state that they find no indication of SO_2 acting as a "Lewis" acid with their indicator, thymol blue.

The addition of small quantities of water to methanol solutions of SO_2 results in the transfer of protons from methanolium ions to water, the water acting as a Bronsted "base".

Kanning, Byrne and Bobalek (J.A.C.S., 66, 1700-03 (1944)) (cf. ibid., 65, 1111-16 (1943)) studied the conductivity of sulfuric acid in methanol, and from their data calculated the dissociation constant of sulfuric acid in methanol. They report the following values:

t, ° C.	K
20	0.027
25	0.024
30	0.024
35	0.018

Although they list two significant figures in the values of the constant at various temperatures, the authors state that the techniques employed can yield only orders of magnitude.

The authors conclude that sulfuric acid in methanol exhibits properties of a strong univalent electrolyte.

Spectrophotometric Estimation of Certain Rare Earth Elements

Therald Moeller

Aqueous solutions of salts of many of the rare earth elements are characterized not only by their very definite absorption spectra but also by the sharpness and intensities of many of the absorption bands in both the visible and infra red regions. A comprehensive spectrophotometric examination of aqueous solutions of the nitrates of most of the rare earth elements (including yttrium) in the spectral range 350 to 100 mμ has been published by Rodden (1,2). Inasmuch as the positions of the absorption bands differ among the various elements and inasmuch as most of the systems obey the Beers relation fairly well, a quantitative method of estimating one material in the presence of others is available. This is particularly true for the determination of a colored substance in the presence of a colorless one such as lanthanum, gadolinium, terbium, yttrium , ytterbium (in the visible), and lutecium, since solutions of the nitrates of these elements show no absorption. The determination of colored components in the presence of each other is easily done if all others exhibit 100% transmittancy at the wave length where one absorbs or if corrections are made by determining the absorptions of all others as pure substances at that desired wave length.

Applications. -- Rodden (1, 2) lists a number of analyses of mixtures, especially of the cerium earths. In brief, the method consists in reducing cerium-free oxides with hydrogen (to convert Pr_6O_{11} to Pr_2O_3) and examining a nitrate solution at 402 mμ (Sm), 446 mμ(Pr), and 521 mμ (Nd). A slight correction for the interference of Sm with the Pr analysis is then made and lanthanum is obtained by difference. This method has been successfully applied in this laboratory through use of General Electric Recording Spectrophotometer (3).

Among the yttrium earths, the chief utility appears to lie in a quantitative following of a fractionation procedure or in the estimation of a colored component in the presence of yttrium. In this laboratory, the ferrocyanide separation of yttrium from erbium (4,5) and the sulfate fractionation of the yttrium earths (4) have been followed, and quantitative analyses of erbium, thulium, and ytterbium samples have been made with excellent and rapidly attainable results.

The effects of certain anions upon these absorption spectra appear to be very pronounced (6); so a standard procedure is necessary.

References:

1. Rodden, C. J.: J. Research Natl. Bur. Stds. 26, 557 (1941).
2. Rodden, C. J.: J. Research Natl. Bur. Stds. 28, 265 (1942).
3. Moeller, T.: Research notes.
4. Kremers, H. E.: Ph. D. Thesis, University of Illinois (1944).
5. Moeller, T., and Kremers, H. E.: J. Am. Chem. Soc. 66, 307 (1944).
6. Edwards, L. J.: B. S. Thesis, University of Illinois (1944).

Diagram of the Corrosion Process — Clifford R. Keizer

1. Ionization of the metal: $Me \longrightarrow Me^+ + e$
2. Passage of metal ions along flaws on surface of metal into solution or of ions in solution in the reverse direction.
3. Removal of metal ions from the surface of the anode by their diffusion into the body of the solution.
4. Motion of the ions in solution under the influence of the electric poles.
5. Diffusion of hydrated hydrogen ions (H_3O^+) toward cathode.
6. Dehydration of H_3O^+.
7. Process of neutralization of hydrogen ions $H^+ + e^- \longrightarrow H$
8. "Malization" of hydrogen atoms $2H \longrightarrow H_2$
9. Diffusion of the hydrogen molecules toward the cathode.
10. Formation of hydrogen bubbles and their release at the surface of the cathode.
11. Passage of oxygen from the air to the electrolyte.
12. Passage of oxygen through the solution by convection.
13. Diffusion of oxygen along the electrolyte layer adjoining the cathode.
14. Reduction of oxygen at the surface of the cathode forming OH^-

$$O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$$

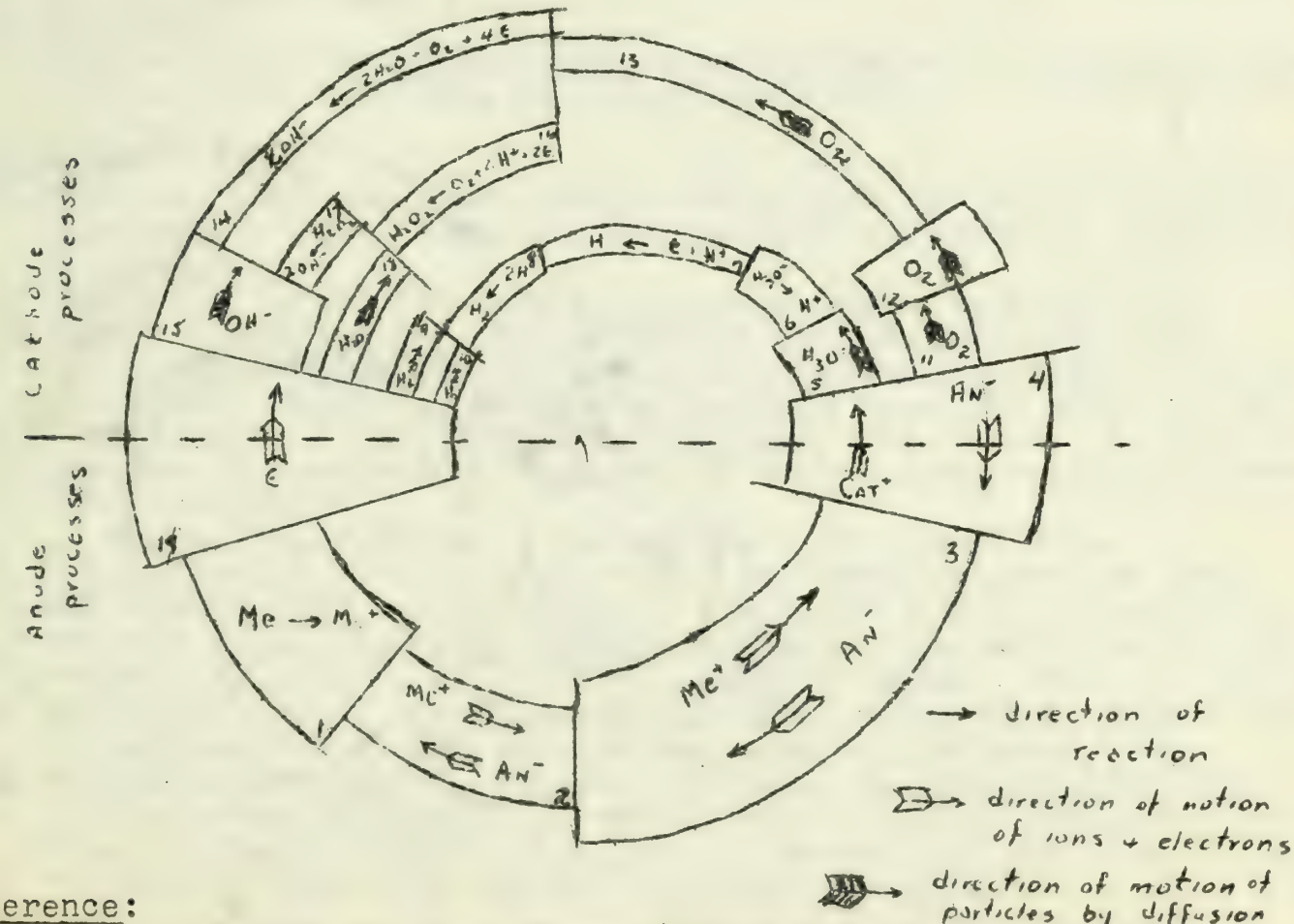
15. Diffusion of OH^- ions from the cathode.
16. Process of reduction of oxygen to hydrogen peroxide

$$O_2 + 2e^- + 2H^+ \longrightarrow H_2O_2$$

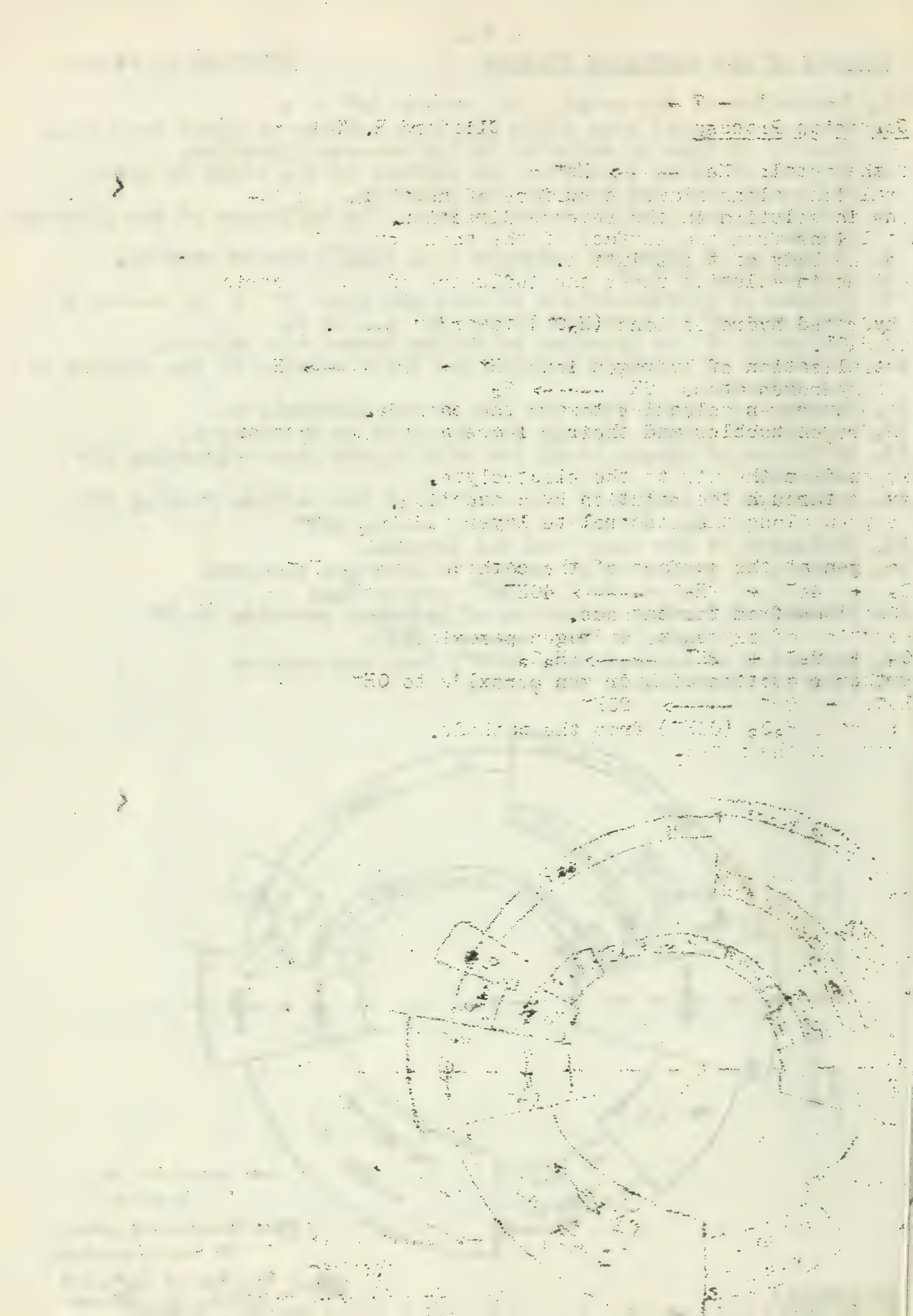
17. Process of further reduction of hydrogen peroxide to OH^-

$$H_2O_2 + 2e^- \longrightarrow 2OH^-$$

18. Diffusion of reduced H_2O_2 ($6OH^-$) from the cathode.
19. Flow of electrons in the metal.



Reference:
N. D. Thomashow, Journ. Gen. Chem. (U.S.S.R.) 12, 585 (1942)



OXIDATION STATES OF COBALT AND NICKEL

John C. Bailar, Jr. November 7, 1944

I. Introduction

A. Methods of Determining Oxidation State

1. Analysis of Compounds. This is misleading unless the structure of the compound is known. Thus, $NiO_2.xH_2O$ exists in two forms -- dioxide and peroxide. The former is black, and contains tetravalent nickel; the latter is green, and contains divalent nickel. It is obtained by the action of H_2O_2 on Ni^{++}, and liberates H_2O_2 when treated with acids. It has never been obtained pure, the Ni:O ratio varying from 1:1.49 to 1:1.98. (1) CoS_2 and NiS_2 do not contain tetravalent metal, but have been shown magnetically to contain divalent metal. (2) They are analagous to pyrite. (3)
2. Properties of the ion in question -- most cobaltic and nickelic compounds are oxidizing agents.
3. Isomorphism with compounds of known oxidation state.
4. Physical methods, such as magnetic susceptibility.

II. Zero-valent and negative valent metals.

A. The carbonyls, nitrosyls, and carbonyl hydrides. If we assume that the electrons in $Ni(CO)_4$ belong to the CO molecules, Ni is zerovalent. If the electrons are partially controlled by the metal, Ni has a negative valence.
Blanchard (4) assumes that in dimeric carbonyls the metal is negative. He believes that an electron is transferred from NO to Co in such compounds as $Co(CO)_3NO$, and from H to Co in $Co(CO)_4H$.

B. Cyanides.
Burgess (5) reduced $K_2Ni(CN)_4$ with potassium in liquid ammonia, and obtained $K_4Ni(CN)_4$ as yellow crystals.

III. Monovalent Metals.

A. Ni_2O has been reported, but probably does not exist. X-ray diagrams indicate only the existence of mixtures of NiO and Ni (14).

B. $K_2Ni(CN)_4$ is reduced by many reducing agents to $K_2Ni(CN)_3$. Alkali metal amalgams are probably best (6,7,8) but zinc, $SnCl_2$ and NaH_2PO_2 can be used. Electrolytic methods are also suitable. $K_2Ni(CN)_3$ readily absorbs O_2 from the air, and in the absence of air, liberates hydrogen from water. In the absence of excess KCN, however, it may be preserved for several days. (8a,8c,9)

$$4K_2Ni(CN)_3 + 2H_2O \text{ --- } 3K_2Ni(CN)_4 + Ni + 2KOH + H_2$$

The oxidation-reduction potential has been measured by Grube and Lieder (10) and by Tedeschi (11). $E^\circ = 0.8?$ volts. It reduces $KMnO_4$, $K_2Cr_2O_7$, H_2O_2(6) and I_2(6) quantitatively. It reduces Ag^+, Hg^{++}, Pb^{++}, Bi^{+++}, As^{+3} to metal. (6)

C. Acidification of solutions of $K_2Ni(CN)_3$ ppts. $NiCN_2$ which can be redissolved in KCN to give the original material. (6)

D. $K_2Ni(CN)_3$ absorbs CO, supposedly giving $K_2[Ni(CN)_3CO]$ (12). It also absorbs C_2H_2 (12), and NO (13). Manchot believes that NO gives $K_2[Ni(CN)_3NO]$, but Job and Samuel say that the NO is reduced to NH_2OH and the Ni^{+1} is oxidized to Ni^{+3}

E. Reduction of Ni^{++} by a mixture of $NaNO_2$ and Na_2SO_2 gives two products, which are said to be $HN(SO_3H)(SO_3Ni).nH_2O$ and $Ni(OH)$. (15) These results seem doubtful.

F. Manchot and his coworkers have prepared many nitrosyl salts, which they claim contain univalent Fe, Co, and Ni. In an atmosphere of NO, cobalt salts react with $K_2S_2O_3$ to give $K_3\ Co(NO)_2(S_2O_3)_2$. The corresponding nickel salt is $K_3\ Ni(NO)(S_2O_3)_2$ (16). Mercaptans can be used instead of thiosulfates (17). The existence of univalent metal in these compounds has been denied by Cambi (18) and by Ormont (19).

IV. Trivalent Metals

A. Many cobalt ammines, cyanides and nitro compounds contain tripositive cobalt.

B. Cobaltic fluoride is readily obtained by the action of fluorine on cobalt salts; has been suggested as a fluorinating agent.

C. Oxidizing agents in alkaline media convert Co^{++} to $Co(OH)_3$. Even air will produce this change to some extent (21). In acid solution it is a powerful oxidizing agent.

D. Cobaltic sulfate can be prepared electrolytically and is a valuable oxidizing agent in organic reactions (22). Cobalt alum is well known (36).

E. Many attempts have been made to prepare $NiCl_3$ (23). Some of these gave red solns. which liberate 0.2-0.3 of an atom of "active" oxygen per nickel atom.

F. $Ni_2O_3.xH_2O$ is doubtful. Alkaline oxidizing agents give precipitates of varying composition, with ratios of Ni:O varying from 1:1.1 to 1:1.9. X-ray data show that these materials are NiO or mixtures of NiO and NiO_2 (24,25). Ott and Cairns, however, believe Ni_2O_3 to be a true compound (31). At lower temperature, NiO absorbs oxygen readily (26).
This material is the oxidizing agent in the Edison storage cell. While it is fairly stable when wet, it loses oxygen slowly in boiling water (27). Tanatar (28) believed it to be a peroxide but this is probably incorrect (29).

G. Schall and coworkers (23a,30) prepared $Ni(C_2H_3O_2)_3$ and $Co(C_2H_3O_2)$ by electrolysis of solutions of the diacetates in glacial acetic acid. The Ni^{+3} compound is deep green and the Co^{+3} compound apple green. They are decomposed by water. This work is rather doubtful, as the authors did not get consistent results.

H. Oxime compounds. Nickel formoxime in alkaline alcohol solutions absorb oxygen from the air to give a deep brown solution. A nickelic complex may be crystallized from the solution (32).

Benzamidoxime forms $\left(C_6H_5C\begin{matrix}NH_2\\NO\end{matrix}\right)_3 Ni$ (33).

V. Tetravalent metals.

A. Nickel dioxide almost certainly exists, although it has never been obtained pure. Preparations having as much as 1.9 atoms of oxygen per nickel atom can be prepared (34.35). It is a strong oxidizing agent, converting chlorides to chlorine, sulfites to dithionate, ammonia to nitrogen.

B. Cobalt dioxide has been reported from oxidation of Co^{++} in alkaline media (37).

C. If an alkaline solution containing Ni is heated with a strong oxidizing agent and dimethylglyoxime, no ppt. forms, but a deep red solution. From this solution, a compound of tetravalent nickel can be crystallized (38). It is said to be $(DH)_2NiO$.

C. (continued)
If a solution of it is acidified in the presence of KI, two equivalents of I_2 are liberated.

D. Polynuclear cobalt ammines. Werner prepared many polynuclear ammines containing peroxo bridges. Analysis indicated that some of these compounds contained both tervalent and tetravalent cobalt. (39) Examples are $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$ and $(NH_3)_4Co\begin{matrix} NH_2 \\ O_2 \end{matrix}Co(NH_3)_5]X_4$. Upon heating with H_2SO_4, such salts are decomposed to mononuclear ammines, with the liberation of gaseous oxygen. The ammount of oxygen liberated indicates one tetravalent cobalt atom. Titration with arsenite leads to the same conclusion (40).
The magnetic susceptibility of these compounds confirms the fact that the ion contains an unpaired electron (40,41) so the assumption of tetravalent cobalt is confirmed.

BIBLIOGRAPHY

1. Pellini and Meneghini, Z. anorg. Chem. 60, 178 (1908); Gazz. chim. ital. 39, I, 163 (1908)
2. Haraldson and Klemm, Z. anorg. allgem. Chem. 223, 409 (1935)
3. de Jong and Willems, Z. anorg. allgem. Chem. 160, 185 (1927)
4. Blanchard, Chem. Reviews 26, 409 (1940)
5. Burgess, Paper read at Boston meeting of American Chemical Society, September, 1939.
6. Moore, Chem. News 68, 295 (1893); 71, 81 (1895)
7. Reitzenstein, Ann. 282, 267 (1894)
8. Bellucci and Corelli, Atti. accad. Lincei 5 22, i, 603, 703 (1913); ii, 485 (1913); Gazz chim. ital. 43, ii, 569 (1913); Z. anorg. Chem. 86, 88 (1914).
9. Bellucci, Gazz. chim. ital. 49, ii, 70 (1919)
10. Grube and Lieder, Z. Elektrochem. 32, 561 (1926)
11. Tedeschi, Atti. accad. Lincei [6] , 23, 894 (1936)
12. Job and Samuel, Compt. rend. 177, 188 (1923)
13. Manchot and Glud, Ber. 59, 2445 (1926)
14. Levi and Tacchini, Gazz. chim. ital. 55, 28 (1925)
15. Tschugaeff and Chlopin, Compt. rend. 159, 62 (1914)
16. Manchot, Ber. 59B, 2445 (1926)
17. Manchot and coworkers, Ber. 60B, 2175, 2318 (1927); 62B, 678, 381 (1929); Ann. 470, 261 (1929).
18. Cambi, Gazz. chim. ital., 59, 56 (1929)
19. Ormont, Acta Physicochim. U.R.S.S. 8, 848 (1938).
20. Ruff, Z. Angew. Chem. 42, 807 (1929); Ruff and Ascher, Z. anorg. allgem. Chem. 183, 193 (1929)
21. Lievin and Herman, Compt. rend. 200, 1474 (1935); Bernard and Job, Compt. rend. 190, 186 (1930)
22. Swann and Xanthakos, J. Am. Chem. Soc. 53, 400 (1931)
23. Schall and coworkers, Trans. Amer. Electrochem. Soc. 45, 161 (1924); Z. Elektrochem. 38, 27 (1932)
24. Clark, Asbury, and Wick, J. Am. Chem. Soc. 47, 2861 (1925)
25. Hendricks, Jefferson and Schultz, Z. Krist. 73, 376 (1930)
26. LeBlanc and Sachse, Z. Elektrochem. 32, 204 (1926)
27. Goralewitsch, J. Russ. phys. chem. Ges. 62, 1577 (1929)
28. Tanatar, Ber. 33, 205 (1900); 36, 1293 (1903); 42, 1516 (1909); 47, 97 (1914)
29. Tubandt and Riedel, Ber. 44, 2565 (1911)
30. Schall and Thieme-Wiedtmarckter, Z. Elektrochem. 35, 337 (1929)
31. Cairns and Ott, Z. Elektrochem. 40, 286 (1934)
32. Hofmann and Ehrhardt, Ber. 46, 1457 (1913)
33. Dubsky and Kuras, Publ. Fac. Sciences Univ. Masaryk, 1929, No. 114; Chem. Listy, 24, 464 (1929)
34. Bellucci and Clavari, Atti. accad. Lincei 5 14, ii, 234 (1905)
35. Bellucci and Clavari, Gazz. chim. ital. 36, i, 58 (1906)
36. Marshall, Proc. Roy. Soc. Edin. 14, 205 (1886-7); Copaux, Ann. chim. phys. 8 , 6, 508 (1905)
37. Metzl, Z. anorg. Chem. 86, 388 (1914)
38. Feigl, Ber. 57B, 758 (1924)
39. Werner, Ann. 375, 1 (1910)
40. Gleu and Rehm, Z. anorg. allgem. Chem. 237, 79 (1938)
41. Malatesta, Gazz. chim. ital. 72, 287 (1942)

THE BASICITY CHARACTERISTICS OF SCANDIUM, YTTRIUM, AND THE RARE EARTH ELEMENTS

Therald Moeller November 14, 1944

I. Introduction

While the term "basicity", as applied to the metallic elements in general, apparently covers all phenomena from the ease with which the free elements lose electrons to the extent to which oxygen containing salts of these elements are decomposed thermally, such phenomena are all manifestations of relative tendencies to lose or gain electrons an are thus reducible to acid-base characteristics in the G. N. Lewis sense.

Scandium, yttrium, and particularly the rare earth elements are generally recognized as yielding the most basic oxides of all the trivalent metals except actinium (11, 21, 69, 71, 73, 93, 99). As evidences of these relatively high basicities, one may cite the ease with which even the strongly ignited oxides dissolve in acids (69, 71, 73), react with ammonium salts both in solution and at elevated temperatures (43, 88), and absorb atmospheric carbon dioxide (69, 71, 73). Parallel evidences of high basicities are noted in the slight, though measurable, hydrolysis of aqueous salt solutions (10, 17, 18, 19, 57, 59, 60, 63, 70, 71, 73, 78, 92, 97) containing weakly basic anions, the comparatively high water solubilities and precipitation pH values of the hydrous oxides and hydroxides (16, 20, 21, 24, 63, 66, 74, 81, 90, 94, 96), the relatively high temperatures required for the decompositions of oxygen-containing salts (102, 103, 104), and the low ionization potentials of the free elements (89).

Significant basicity differences, especially between scandium and yttrium, yttrium and lanthanum, and lanthanum and lutecium, are apparent. Because of the excellent agreement between theoretically predicted basicity variations and those observed and because of the dependence of many separational procedures upon such basicity differences, a detailed examination of these phenomena is profitable.

II. Establishment of Relative Basicities

A. Theoretical Considerations.

Since the relative attractions for electrons are dependent upon atomic and ionic sizes (99), basicity predictions can be based upon size considerations. Atomic and molecular volumes for most of the elements and many of their compounds have been reporte (6, 12, 13, 15, 44, 45, 46, 56, 62, 98). Data in Table I indicat the expected increases from scandium through yttrium to lanthanum. The decrease between lanthanum and lutecium (the lanthanide contraction) is ascribable to the increased nuclear charges and the simultaneous filling of the 4f orbitals. Paralleling atomic and molecular size variations are variations in the radii of the trivalent ions, the empirical and calculated values for which are listed. Basicity decreases should parallel size decreases. The combined effects of cation charge and size are given by the ionic potentials of Cartledge (35), and the relation between size and ionization potential is apparent.

Size and charge-size considerations would predict lower basicities for materials in a +4 oxidation state and higher basicities for those in a +2 state. The reported amphoterism of CeO_2 (26, 95), $PrO_{1.8}$ (4), and Tb_4O_7 (4) and the ease of hydrolysis of Ce(IV) salts (9, 22, 55, 93) confirm the lowered basicities of high valent materials. Although amphoterism has been reported for La_2O_3 (3), this is doubtful (105).

B. Experimental Establishment of Relative Basicities

1. Order of Precipitation by Alkalies. From a mixture of rare earth salts in solution, soluble alkalies will precipitate the least basic materials first. Scandium has thus been shown to be the weakest base, and basicity decreases from lanthanum down through lutecium (11, 71, 73, 92, 93). Yttrium, however, appears to be as highly basic as the cenium earths, a position which may be ascribable to a concentration effect (96). Early work showed gadolinium to be more basic than samarium (5, 8, 30), but more careful procedures have reversed this order (47).

2. Precipitation and Dissolution of Hydrous Oxides and Hydroxides. Solubility studies (24, 39, 64) and electrometric measurements upon alkali titrations (16, 20, 21, 66, 74, 81, 90, 94) have indicated decreasing basicities in the series lanthanum to lutecium, with yttrium occupying a place close to holmium and scandium following lutecium. Comparisons of solubility product constants, assuming the precipitation of hydrous hydroxides (54, 101), have lead to an order of comparative basicities paralleling an order of comparative ionic radii (39, 74). (See Table I)

3. Hydrolysis Studies. The hydrolysis of rare earth salt solutions has been measured by determination of conductivities (10, 17, 18, 57, 70), by measurement of hydrogen ion concentration (10, 60, 78), by determination of free acid through extraction (97), and by the effects of the liberated hydrogen ion upon the hydrolysis of esters (17, 18, 70), the inversion of sucrose (18), and the reduction of iodate with iodide (59). In addition the evolution of carbon dioxide from hydrolyzed carbonates has been measured (19). Precipitation of basic salts, for example nitrites, has been investigated (53, 92).

4. Thermal Decompositions to Basic Salts or Oxides. Measurement of the decomposition temperatures of the anhydrous sulfates (102, 103, 104) has shown that decomposition temperature rises with increasing basicity of the element concerned. Such basicity series do not agree too well with those arrived at by other means.

5. Thermo-Chemical Investigations. The heat of reaction of the trivalent oxide with hydrochloric acid has been found to increase in the series samarium, neodymium, praseodymium, lanthanum (72).

6. Electrode Potentials. Although no direct relation exists between basicity and electrode potential, Hcyrovsky (49) has derived an expression relating basicity, electrode potential, and cation mass. The only measurements approaching electrode potentials are the polarographic data of Noddack and Brukl (80), but although these authors point out a basicity relation, it appears that a portion of their data represents reduction of the hydrogen ion (50, 64) and application of their figures to the Hcyrovsky relation is impractical. The approximate potentials listed by Latimer (68) indicate lanthanum to be the most basic and scandium the least.

C. Summary

Basicity summaries based upon a variety of results (1, 11, 19, 21, 39, 51, 59, 60, 61, 69, 71, 73, 74, 92, 99) indicate basicity to decrease in the order La, Ce(III), Pr, Nd, Il, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu, Sc, Ce(IV).

II. Separations Based upon Basicity Differences

Procedures of this type have been most successful in the removal of lanthanum, cerium, thorium, and scandium and in a preliminary fractionation of the yttrium sub-group. Although any precipitation method may, in a sense be regarded as a basicity method, only those directly involving the hydrogen or hydroxyl ions need be listed. Typical procedures are:

1. Precipitation by Alkaline Materials. The caustic alkalies (5, 8, 16, 30), ammonia (5, 8, 33, 42, 52, 82-87, 91, 95), magnesia (76, 91) rare earth oxides (100), organic bases (48, 58), oxides and carbonates (78), and urea (41, 91) have been employed. The controllable pH achieved in urea (41) and in ammonia systems containing complex-forming cations or ammonium salts (82-87) have proved useful.

2. Hydrolysis. Oxidation of cerium followed by hydrolysis is the common method for removing this element (22, 23, 69, 71, 73, 75). Fractional hydrolysis of such salts are the azides (1, 29, 32, 34) and the nitrites (14, 52, 53, 92) has yielded excellent results, especially in yttrium sub-group separations.

3. Hydrolysis by Means of Electrolysis. First employed by Krüss (67), electrolysis of mixed salt solutions, usually with mercury cathodes, has given excellent results (2, 33, 35-37, 65, 77, 91), the least basic materials separating first.

4. Fractional Solution of Oxides Acids. Although not widely applied, this procedure has been used with some success (26, 42, 75).

5. Fractional Thermal Decomposition of Oxygen-Containing Salts. Favored among such procedures is the nitrate fusion process of Berlin (7) which has been employed by many workers, especially in the separation of the yttrium earths (14, 27, 28, 31, 38, 40, 55, 79). Thermal decomposition of sulfates at controlled temperatures has not proved effective (102).

Summary of Properties

Symbol	At. No.	Mol. Vol -- cc.		Rad. of R^{+++} Å		Ionic Pot. (25)	Atomic Vol.-cc. (13,62)	Ioniz. Pot.—e.v. (89)	Pptn. pH (66)	Soly. of $R(OH)_3$ x10^6 (74)	Basicity of $R(OH)_3$ rel. to $Y(OH)_3$	
		R_2O_3 (45)	$R_2(SO_4)_3.8H_2O$	Emp. (44)	Calc. (46)						(39)	(74)
La	57	50.28[x]	---	1.22	1.004	2.46	22.43	5.49	7.82	7.8	1300	1235
Ce	58	47.89[x]	---	1.18	0.939	2.54	20.70	----	7.60	4.8	---	185
Pr	59	46.65[x]	253.9	1.16	0.910	2.58	20.79	5.76	7.35	5.4	80	333
Nd	60	46.55[x]	252.4	1.15	0.900	2.61	20.62	6.31	7.00	2.7	47	23.5
Il	61	------	-----	----	-----	----	-----	----	----	---	---	---
Sm	62	48.38	247.9	1.13	0.872	2.65	21.70	6.55	6.92	2.0	---	8.4
Eu	63	48.28	247.3	1.13	0.871	2.65	29.00	----	6.82	1.4	---	4.2
Gd	64	47.58	246.4	1.11	0.861	2.70	19.79	6.65	6.83	1.4	3.4	2.6
Tb	65	46.38	-----	1.09	0.845	2.75	19.11	6.74	----	---	---	---
Dy	66	45.49	242.8	1.07	0.832	2.80	18.97	6.82	----	---	0.5	---
Y	39	45.13	240.8	1.06	0.827	2.83	20.46	----	6.95	1.2	1.0	1.0
Ho	67	44.89	241.1	1.05	0.823	2.86	18.65	----	----	---	---	---
Er	68	44.38	239.3	1.04	0.816	2.88	18.29	----	6.76	0.8	---	0.16
Tm	69	44.11	-----	1.04	0.812	2.88	18.12	----	6.40	0.6	---	0.041
Yb	70	42.5	235.1	1.00	0.789	3.00	24.76	7.06	6.30	0.5	---	0.036
Lu	71	42.25	234.7	0.99	0.785	3.03	17.96	----	6.30	0.5	---	0.031
Sc	21	35.53 xA	-----	0.83	0.681	3.62	-----	----	6.10° °(94)	---	---	---

IV. References

1. Ant-Wuorinen, J.: Teknillinen Aikakauslehti 21, 365 (1931).
2. Ant-Wuorinen, J.: Suomen Kemistilehti 13B, 1, (1940).
3. Baskerville, C., and Catlett, G. F.: J. Am. Chem. Soc. 26, 75 (1904
4. Beck, G.: Angew. Chem. 52, 536 (1939)
5. Benedicks, C.: Z. anorg. Chem. 22, 393 (1900)
6. Benedicks, C.: Z. anorg. Chem. 39, 41 (1904)
7. Berlin, N. J.: Forhandl, Scand. Naturf. Kjöbenhaven 8, 448 (1860)
8. Bettendorff, A.: Ann. 270, 376 (1892)
9. Biltz, W.: Ber. 35, 4431 (1902)
10. Bodländer, E.: Inaug. Dissert. Berlin, (1915)
11. Böhm, C. R.: "Die Darstellung der seltenen Erden", Erster Band, pp. 35-244. Verlag von Veit Comp., Leipzig (1905)
12. Bommer, H.: Z. anorg. allgem. Chem. 241, 273 (1939)
13. Bommer, H.; and Hohmann, E.: Z. anorg. allgem. Chem. 241, 268 (1939
14. Boss, A.E.; with Hopkins, B S.: J. Am. Chem. Soc. 50, 298 (1928)
15. Bourion, M. F.: Ann. chim. phys. 21, 83 (1910)
16. Bowles, J. A. C., and Partridge, H. M.: Ind. Eng. Chem., Anal. Ed. 9, 124 (1937)
17. Brauner, B.: Z. Elektrochem. 14, 525 (1908)
18. Brauner, B., and Svagr, E.: Collection Czechoslov. Chem. Communication, 4, 49, 239 (1932)
19. Brinton, P. H. M.-P., and James, C.: J. Am. Chem. Soc. 43, 1446 (1921)
20. Britton, H.T.S.: J. Chem. Soc. 127, 2142 (1925)
21. Britton, H.T.S.: "Hydrogen Ions", 3rd Ed., Vol.II, pp. 63-65, 79-84. Chapman and Hall, Ltd., London (1942)
22. Browning, P. E., and Roberts, E. J.: Am. J. Sci. [IV], 29, 45 (1910)
23. Bunsen, R.: Ann. 105, 40 (1858)
24. Busch, W.: Z. anorg. allgem. Chem. 161, 161 (1927)
25. Cartledge, G. H.: J. Am. Chem. Soc. 50, 2855, 2863 (1928)
26. Chase, W. S.: Ind. Eng. Chem. 8, 239 (1916)
27. Cleve, A.: Z. anorg. Chem. 32, 129 (1902)
28. Cleve, P. T., and Hoeglund, O.: Bull. soc. chim. [ii], 18, 193, 289 (1872)
29. Curtius, T., and Darapsky, A.: J. prakt. Chem. [ii], 61, 408 (1900)
30. de Boisbaudran, L.: Compt. rend. 111, 393 (1890)
31. Debray, H.: Compt. rend. 96, 828 (1883)
32. Dennis, L. M.: J. Am. Chem. Soc. 18, 947 (1896)
33. Dennis, L. M., and Dales, B.: J. Am. Chem. Soc. 24, 401 (1902)
34. Dennis, L. M., and Kortright, F. L.: Am. Chem. J. 16, 79 (1894)
35. Dennis, L. M., and Lemon, B. J.: J. Am. Chem. Soc. 37, 131 (1915)
36. Dennis, L. M., and Ray, A. B.: J. Am. Chem. Soc. 40, 174 (1918)
37. Dennis, L. M., and van der Meulen, P. A.: J. Am. Chem. Soc. 37, 1963 (1915)
38. Driggs, F. H., with Hopkins, B S.: J. Am. Chem. Soc. 47, 363 (1925
39. Endres, G.: Z. anorg. allgem. Chem. 205, 321 (1932)
40. Engle, E. W., and Balke, C. W.: J. Am. Chem Soc. 39, 53 (1917)
41. Fogg, H. C., and Hess, L.: J. Am. Chem. Soc. 58, 1751 (1936)
42. Frerichs, F. and Smith, F.: Ann. 191, 331 (1878)
43. Gibbs, W.: Proc. Amer. Acad. 28, 260 (1893)
44. Goldschmidt, V. M.: Ber. 60, 1263 (1927)
45. Goldschmidt, V. M., Barth, T., and Lunde, G.: Skrifter Norske Videnskaps. Acad. Oslo, 1 Mat.-Nat. Kl. 1925, No. 7.
46. Grimm, H. G., and Wolff, H.: Z. phys. Chem. 119, 254 (1926)
47. Günther, P., Kotowski, A., and Lehl, H.: Z. anorg. allgem. Chem. 200, 287 (1931)

48. Hartwell, B. L.: J. Am. Chem. Soc. 25, 1128 (1903)
49. Heyrovský, J.: Proc. Roy. Soc. A102, 628 (1923)
50. Heyrovský, J.: "Fortschritte der Polarographie 1936-1938", Dritter Teil of Böttger's "Physikalische Methoden der analytischen Chemie", p. 443. Akademische Verlagsgesellschaft m.b.h., Leipzig (1939).
51. Hopkins, B S.: J. Chem. Education 13, 363 (1936)
52. Hopkins, B S., and Balke, C. W.: J. Am. Chem. Soc. 38, 2332 (1916)
53. Hughes, G., and Hopkins, B S.: J. Am. Chem. Soc. 55, 3121 (1933)
54. Hüttig, G. P., and Kantor, H.: Z. anorg. allgem. Chem. 202, 421 (1931)
55. James, C.: J. Am. Chem. Soc. 34, 757 (1912).
56. Jantsch, G.: Z. anorg, Chem. 76, 303 (1912)
57. Jantsch, G., Grubitsch, H., and Lischka, E.: Z. Elektrochem. 43, 293 (1937).
58. Jefferson, A. M.: J. Am. Chem. Soc. 24, 540 (1902)
59. Katz, S. H., and James, C.: J. Amer. Chem. Soc. 36, 779 (1914)
60. Kleinheksel, J. H., with Kremers, H. C.: J. Am. Chem. Soc. 50, 959 (1928)
61. Klemm, W.: Angew. Chem. 51, 577 (1938)
62. Klemm. W., and Bommer, H.: Z. anorg. allgem. Chem. 231, 138 (1937)
63. Kolthoff, I. M., and Elmquist, R.: J. Am. Chem. Soc. 53, 1217 (1931)
64. Kolthoff, I. M., and Lingane, J. J.: "Polarography", pp. 153, 304-306. Interscience Publishers, Inc., New York (1941)
65. Kremers, H. C.: and Quill, L. L.: Trans. Am. Electrochem. Soc. 55, 199 (1929)
66. Kremers, H. E.: Thesis, University of Illinois (1944).
67. Krüss, G.: Z. anorg. Chem. 3, 60 (1893)
68. Latimer, W. M.: "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions", pp. 265-269. Prentice-Hall, Inc., New York (1938)
69. Levy, S. I.: "The Rare Earths", Edward Arnold, London (1915)
70. Ley, H.: Z. phys. Chem. 30, 193 (1899)
71. Little, H.F.V.: "A Textbook of Inorganic Chemistry", edited by J. N. Friend, Vol. IV. Charles Griffin and Company, Ltd., London (1917)
72. Matignon, C.: Ann. chim. phys. [viii], 8, 243, 386, 402, 426 (1906)
73. Mellor, J. W.: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 5, pp. 494-709. Longmans, Green and Co., London (1924)
74. Moeller, T., and Kremers, H. E.: J. Phys. Chem. 48, (1944).
75. Mosander, C. G.: Pogg. Ann. [ii], 60, 297 (1843)
76. Muthmann, W., and Rolig, H.: Ber. 31, 1718 (1898)
77. Neckers, J. W., with Kremers, H. C.: J. Am Chem. Soc. 50, 950 (1928)
78. Neish, A. C., and Burns, J. W.: Can. Chem. Met. 5, 69 (1921)
79. Nilson, L. F.: Ber. 12, 554 (1879)
80. Noddack, W., and Brukl, A.: Angew, Chem. 50, 362 (1937)
81. Oka, Y.: J. Chem. Soc. Japan 59, 971 (1938)
82. Prandtl, W.: Z. anorg. allgem. Chem. 143, 277 (1925)
83. Prandtl, W.: Z. anorg, allgem. Chem. 209, 13 (1932)
84. Prandtl, W.: and Huttner, K.: Z. anorg. allgem. Chem. 136, 289 (1924)
85. Prandtl, W., and Lösch, J.: Z. anorg. allgem. Chem. 122, 159 (1922); 127, 209 (1923)
86. Prandtl, W., and Rauchenberger, J.: Ber. 53, 843 (1920)
87. Prandtl, W., and Rauchenberger, J.: Z. anorg. allgem Chem. 120, 120 (1922); 122, 311 (1922); 129, 176 (1923)
88. Reed, J. B., Hopkins, B S., and Audrieth, L. F. : J. Am. Chem. Soc. 57, 1159 (1935)

89. Rolla, L., and Piccardi, G.: Phil. Mag. [vii], 7, 286 (1929)
90. Sadolin, E.: Z. anorg. allgem. Chem. 160, 133 (1927)
91. Selwood, P. W.: J. Am. Chem. Soc. 55, 4300 (1933)
92. Sherwood, G. R., and Hopkins B S.: J. Am. Chem. Soc. 55, 3117 (1933)
93. Spencer, J. F.: "The Metals of the Rare Earths", Longmans, Green and Co., London (1919)
94. Sterba-Böhm, J. S., and Melichar, M.: Collection Czechoslov. Chem. Communications 7, 57, 131 (1935)
95. Trombe, F.: Compt. rend. 215, 539 (1942)
96. Trombe, M.: Compt. rend. 216, 888 (1943)
97. Vesterberg, K. A.: Svensk Kem. Tidskrift 29, 101 (1917)
98. von Hevesy, G.: Z. anorg. allgem. Chem. 147, 217 (1925); 150, 68 (1925)
99. von Hevesy, G.: "Die seltenen Erden vom Standpunkte des Atombaues", Verlag von Julius Springer, Berlin (1927)
100. von Welsbach, A.: Monatsh. 5, 508 (1884)
101. Weiser, H. B., and Milligan, W. O.: J. Phys. Chem. 42, 673 (1938)
102. Willard, H. H., and Fowler, R. D.: J. Am Chem. Soc. 54, 496 (1932)
103. Wöhler, L., and Flick, K.: Ber. 67B, 1679 (1934)
104. Wöhler, L., and Grünzweig, M.: Ber. 46, 1726 (1913)
105. Zambonini, F., and Carobbi, G.: Gazz. chim. ital. 54, 46 (1924)

THE OXIDATION-REDUCTION POTENTIALS OF VANADIUM

H. A. Laitinen November 21, 1944

I. Introduction.

Vanadium exists in aqueous solution in the oxidation states 2, 3, 4 and 5. Including the metal itself, there are five oxidation states to be considered, and therefore four oxidation-reduction couples for which electrode potentials can be given.

Theoretically, it would be advantageous to write two electrode reactions for each couple, corresponding to the behavior in acid and alkaline solution. Measurements have been made in acid solution for the couples 2,3; 3,4 and 4,5. In alkaline solution, no measurements have been made, and the solubilities of the hydroxides $V(OH)_2$, $V(OH)_3$ and $VO(OH)_2$ are not known. Moreover, the formation of polyvanadates makes the +5 oxidation state extremely complex in any but strongly acid solution. The discussion will, therefore, be limited to the measurement of the three couples noted above in acid solution, and to an estimation of the potential of the couple V, V^{++} from heat and entropy data.

I. The vanadium (IV) - vanadium (V) couple.

Several measurements of cells involving tetravalent and pentavalent vanadium have been made (1, 2, 3, 4). Foerst and Böttcher (2) give evidence for a half-cell reaction,

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{++} + H_2O \qquad (1)$$

but uncertain liquid junction potentials diminish the reliability of the measurements. Coryell and Yost (3) have eliminated the liquid junction potential by measuring the cell

$$Pt,\ VO_2^+(C_1) + VO^{++}(C_2) + HCl(C_3),\ HCl(C_3),\ Hg_2Cl_2,\ Hg \qquad (2)$$

but regard the pentavalent vanadium to exist predominantly as HVO_3, giving the electrode reaction

$$HVO_3 + 3H^+ + 3e^- \rightleftharpoons VO^{++} + 2H_2O$$

Solubility data (5) (3) of V_2O_5 in HNO_3, HCl and $HClO_4$ indicate that the pentavalent vanadium is present as VO_2^+ or its equivalent $V(OH)_4^+$. Carpenter (4) made measurements which confirmed the half-cell reaction (1) and recalculated the data of Coryell and Yost on the same basis.

The E.M.F. of cell (2) was extrapolated to zero concentration keeping $C_2/C_1.C_3$ constant. Correcting for the potential of the calomel electrode gave $E^\circ = -1.00$ volt.

The vanadium (III) - vanadium (IV) couple.

Rutter (1) measured the E.M.F. of the cell

$$Pt,\ VOSO_4 + V_2(SO_4)_3 + H_2SO_4(0.25\underline{M}),\ H_2SO_4(0.25\underline{M}),\ Hg_2SO_4,\ Hg$$

keeping the total vanadium concentration 1M, varying the ratio of V(III) to V(IV) over wide limits. Based upon these measurements, Abegg, A erbach and Luther (6) give $E^\circ = -0.4$ volt for the reaction

$$V^{+++} + H_2O \rightleftharpoons VO^{++} + 2H^+ + 2e^- \qquad (4)$$

whereas Gerke (7) computes

$$1/2(VO)_2SO_4 + 1/2SO_4^{=} \;=====\; VOSO_4 + e^-,\ E^\circ = -0.30 \text{ volt} \quad (5)$$

Foerster and Böttcher (2) measured a similar cell with V(III) and V(IV) concentrations kept equal. The total V concentration and H_2SO_4 concentration were varied but the latter was not kept equal on the two sides of the cell. Hence, a liquid juction potential was included. Latimer (8) gives $E^\circ = -0.314$ volt with a reference to Foerster and Böttcher.

The best measurements are those of Jones and Colvin (9) who measured the E.M.F. of a series of cells

$$Pt,\ VOSO_4(C_4) + 1/2V_2(SO_4)_3(C_3) + H_2SO_4(C_1),\ H_2SO_4(C_1),\ Hg_2SO_4,\ Hg$$

1. keeping C_1 constant, varying C_4/C_3.

2. keeping $C_4/C_3 = 1$, varying C_1 from 1 to 0.02

The results were calculated by

1. extrapolating E.M.F. to zero vanadium concentration, at each acid concentration.

2. extrapolating to zero concentration of vanadium and acid (zero ionic strength) using the Debye-Hückel theory as a guide. The result is that $E^\circ = -0.337$ volt at 25°.

IV. The vanadium (II) - vanadium (III) couple.

The history of the investigation of the vanadous-vanadic couple parallels closely that of the vanadic-vanadyl couple. The earliest study was that of Rutter (13) who measured the EMF. of the cell

$$Pt,\ 1/2V_2(SO_4)_3 + VSO_4 + H_2SO_4(0.25\underline{M}),\ H_2SO_4(0.25\underline{M}),\ Hg_2SO_4, Hg$$

and found a value of $E^\circ = +0.210$ volt.

Foerster and Böttcher (2) also made some similar measurements. They found that variable potentials were obtained when using platinum electrodes owing to the evolution of hydrogen but that if mercury electrode is used, the difficulty is eliminated. This "mixed potential" behavior of electrodes has been described in other cases (10, 11). However, Foerster and Bottcher failed to remove the liquid junction potential.

Jones and Colvin (12) measured the E.M.F. of the cell

$$Hg,\ 1/2V_2(SO_4)_3(C_3) + VSO_4(C_2) + H_2SO_4(C_1),\ H_2SO_4(C_1),\ Hg_2SO_4,\ Hg.$$

and calculated the results in much the same way as explained above for the vanadic-vanadyl couple. They found that $E^\circ = +0.255$ volt at 25°.

V. The vanadium - vanadium (II) couple

The potential of this couple has never been measured, and the measurement in aqueous solution appears to be impossible. In acid solution, the metal would rapidly react with hydrogen, if its behavior were reversible. Actually, it does not give reversible electrode behavior either in acid or alkaline solution.

Latimer (8) estimates from the free energy of formation of vanadous oxide and the free energy of solution of the oxide in acid, a value of $E° = Ca.\ 1.8$ volts. From the heat of hydration of vanadous oxide and the solubility of vanadous hydroxide, a value of $E° = Ca\ 1.2$ volts is estimated. A final estimate of 1.5 ± 0.3 volt is given. No source of the data is indicated, except for the heat of formation data which were listed by Bichowsky and Rossini (14).

The following sample calculation will serve to illustrate the estimation of the electrode potential in cases where experimental data are scanty.

Given that the heat of formation of V_2O_2 is -195 kcal. (14,15) and estimating the entropy of V_2O_2 to be twice that of MnO (16) which is 14.4 cal./deg. mole, the free energy of formation of V_2O_2 is -185 kcal., compared with Latimer's(8) value of 182 kcal.

To estimate the free energy of the reaction

$$V_2O_2 + 4H^+ \longrightarrow 2V^{++} + 2H_2O \qquad (6)$$

we will first find the heat of reaction between MnO and HCl or HNO_3. The heats of formation of $MnCl_2$ (aq) (17), MnO (S) (18) and HCl (aq) (19) are respectively 128.7, 96.5 and 39.7 kcal./mole., giving a heat of reaction of -47.2 kcal. Using $Mn(NO_3)_2$(aq) (17) and HNO_3 (aq) (14), the heats of formation are 147.8 and 49.2 kcal. giving a heat of reaction of -47.1 kcal. for the reaction.

$$MnO + 2H^+ \longrightarrow Mn^{++} + H_2O$$

Apparently, no entropy data exist for Mn^{++}, but for the analagous reaction of FeO to give Fe^{++}, the entropy of H^+ is zero by convention, that of Fe^{++} is -25.9 (20), that of H_2O is 16.75 (21,22) and that of FeO is 14.2 cal./mole deg. (16). The entropy change is -23.4. Assuming for the V_2O_2 reaction an entropy change of twice this amount, the free energy change of reaction (6) becomes 80 kcal. Subtracting the free energy of formation of two moles of water we have

$$\begin{array}{lllllll}
2V & + & O_2 & \longrightarrow & V_2O_2 & & \Delta F° = -185 \\
V_2O_2 & + & 4H^+ & \longrightarrow & 2V^{++} & + \ 2H_2O & \Delta F° = -\ 80 \\
2H_2O & & & \longrightarrow & 2H_2 & + \ O_2 & \Delta F° = \ 113 \\
\hline
2V & + & 4H^+ & \longrightarrow & 2V^{++} & + \ 2H_2 & \Delta F° = -152 \text{ kcal.}
\end{array}$$

The standard potential is calculated from the equation

$$E° = -\Delta F°/nF = 152/4 \times 23.06 = 1.7 \text{ volts.}$$

BIBLIOGRAPHY

1. T. F. Rutter, Z. anorg. Chem. 52, 377 (1907)
2. F. Foerster and F. Böttcher, Z. physik. chem. 151A, 321 (1930)
3. C. D. Coryell and D. M. Yost, J. Am. Chem. Soc. 55, 1909 (1933)
4. J. E. Carpenter, J. Am. Chem. Soc. 56, 1847 (1934)
5. J. Meyer and M. Aulich, Z. anorg. allgem. Chem. 194, 282 (1930)
6. R. Abegg, F. Auerbach and R. Luther, "Messungen elektromotorische Krafte galvanische Ketten", W. Knapp, Halle, 1911, p. 204.
7. "International Critical Tables", Vol. VI, 332 (1929)
8. W. M. Latimer, "Oxidation Potentials", Prentice-Hall, New York, 1938, p. 243
9. Grinnell Jones and J. H. Colvin, J. Am. Chem. Soc. 66, 1563 (1944)
10. I. M. Kolthoff and C. S. Miller, J. Am. Chem. Soc. 62, 2171 (1940)
11. H. A. Laitinen, J. Am. Chem. Soc. 64, 1133 (1942)
12. Grinnell Jones and J. H. Colvin, J. Am. Chem. Soc. 66, 1573 (1944)
13. T. F. Rutter, Z. anorg Chem. 52, 373 (1907)
14. F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances", Reinhold, New York, 1936.
15. W. G. Mixter, Am J. Sci. (4) 34, 141 (1932)
16. K. K. Kelley, U. S. Bur. of Mines Bull., No. 394 (1935)
17. H.P.J.J. Thomsen, "Thermochemische Untersuchungen", Barth, Leipzig, (1882-6)
18. W. A. Roth, Z. angew. Chem. 42, 981 (1929)
19. F. D. Rossini, Bur. Standards J. Research 6, 791 (1931)
20. W. M. Latimer, K. S. Pitzer and W. V. Smith, J. Am. Chem. Soc. 60, 1829 (1938)
21. W. F. Giauque and J. W. Stout, J. Am. Chem. Soc. 58, 1144 (1936)
22. W. F. Giauque and R. C. Archibald, J. Am. Chem. Soc. 59, 561 (1937)

THE HONORABLE ROBERT BOYLE

Virginia Bartow November 28, 1944

I. Youth 1626-1644
   1. Born, Lismore, Ireland, a fourteenth child, January 25, 1626.
   2. Mother, Katherine Fenton, daughter of Sir Geeffrey Fenton, Secretary of State for Ireland.
   3. Father, Richard Boyle, the Great Earl of Cork, Lord Justice of Ireland -- Elizabethan, Protestant, Royalist -- "the richest man in Great Britain and the most influential in Ireland".
   4. Family, eleven brothers and sisters completely involved in the court, the society and political struggles of the period.
   5. Training
      a. Foster parents -- Irish peasants
      b. Eton -- tutor under Sir Henry Wottan, cousin of Francis Bacon
      c. Geneva -- tutor a strict Calvinist.
      d. Italian travels -- Florence at end of the life of Galelio.

II. Period of study and apprenticeship 1644-1660
   1. English Civil War, Parlimentary Rule
   2. Politics -- a cavalier -- sympathy with the Commonwealth.
   3. Abode -- Stallbridge Manor
      a. Gentleman farmer
      b. Experimentalist and Philosopher
      c. Alchemist
   4. London -- with Lady Ranelagh, Katherine Boyle, a Parlimentarian.
      a. The "Invisible College", Wallis, Willis, Wren, Barlow, Hooke, Evelyn.
      b. Milton

   5. Oxford, study of natural science -- the Purge -- Bodleian Library.
   6. Publications of importance
      "Occasional Reflections"
      "Seraphic Love"
      "Some Considerations concerning the Style of the Holy Bible"
      "The Martyrdom of Theodora and Didymus"

II. Period of Productivity 1660-1670
   1. Restoration
   2. The Plague and The Fire
   3. The Royal Society
   4. Publications
      1660 "The Spring of the Air"
      1661 "The Skeptical Chemist"
      Numerous Scientific Papers on Color, Cold, Corpuscular Theory, etc.

IV. Last Years 1670-1691
1. Abode -- London on Pall Mall -- ill health
2. Religious views -- leader of Anglican Church, the "via media" between Romanism and Protestantism
3. Positions offered and rejected.
   a. Peerage by Charles II
   b. High Place in the church upon taking holy orders.
   c. Presidency of the Royal Society
   d. Provost of Eton
4. Positions held
   a. Governorship for the Society for the Propagation of the Gospel in New England
   b. Membership on the Company of the Royal Mines
   c. Director of the East India Company
   d. Oxford, Doctor of Physic
5. Achievements
   a. "Father of Chemistry"
      1. An Historian
      2. Founder of analytical chemistry
      3. Clear enunciation of the idea of chemical elements
      4. Proof air needed for combustion
   b. Discoverer with Hooke of the Ideal Gas Law
   c. Supersederof scholasticism of Aristotle and medieval philosophy of Paracelsus with Baconian induction or the "New Philosophy".
   d. Purpose -- "To consecrate his scientific labors for a witness to God's creation and governance of the universe."
6. Death -- London, at Lady Ranelagh's December 30, 1691.
   a. Boyle Lectureship
   b. "Not sure science is good for world."

BIBLIOGRAPHY

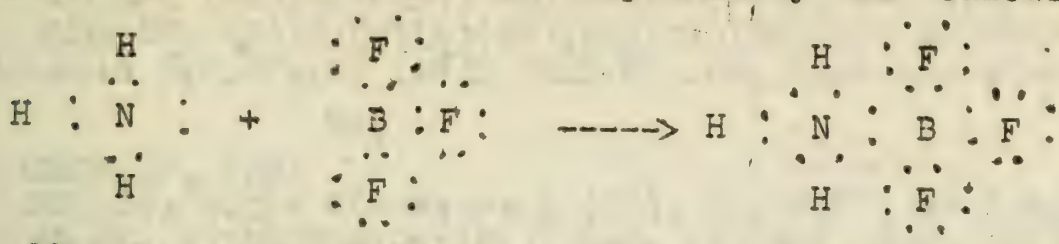
Books
Townshend, Dorothea, "The Life and Letters of the Great Earl of Cork", Duckworth and Company, London, 1904.
Masson, Flora, "Robert Boyle", Constable and Company, London, 1914.
More, Louis Trenchard, "The Life and Works of the Honorable Robert Boyle", Oxford University Press, New York, New York, 1944.
Shaw, Peter, "The Philosophical Works of the Honorable Robert Boyle, Esq.", W. and J. Innys, London, 1725.

Essays
Thorpe, Sir Edward, "Essays in Historical Chemistry", Macmillan Company Ltd., London 1931, Chapter I.
Ramsay, Sir William, "Essays Biographical and Chemical", Archibald, Constable and Company, Ltd., London 1908, p. 19-30.
Tilden, Sir William A. "Famous Chemists, the Men and Their Work", George Routledge and Sons, Ltd., London, 1931, Chapter I.

COORDINATION COMPOUNDS OF BORON TRIFLUORIDE

Donald Ray Martin December 5, 1944

Although boron trifluoride was discovered over one-hundred and thirty years ago (35), knowledge of the many coordination compounds, which it is capable of forming, is comparatively recent. On the basis of the electronic structure of boron trifluoride, the boron atom should be a good acceptor of electrons and boron trifluoride should form many coordination compounds by the following mechanism:



Actually the number of such compounds is astonishingly great while the number of different atoms, which have been found to donate to the boron atom, is surprisingly small.

These addition compounds will be discussed according to the groups in the Periodic Table of which the donor atom is a member.

Group 0. Argon has been found by Booth and Willson (15) to form six coordination compounds with BF_3 at low temperatures under pressure. See Table I.

Groups I, II, III. As would be expected from the fact that they are polar, none of the members of these groups have been reported as donors to the boron atom of BF_3.

Group IV. Although no coordination compounds have been isolated in which the donor atom is a member of Group IV, it has been postulated that the carbon atom, in olefin compounds, is the donor to the boron atom of BF_3 in condensation and polymerization reactions in which BF_3 is the catalyst (11) (33) (36) (52) (55) (56) (77).

BF_3 has been reported to be unreactive toward CH_4, closed chain compounds, e.g. C_6H_6 and CO (33).

Krause and Knobbe (47) reported a reaction between a saturated hydrocarbon and BF_3 in which tertiary butyl boron fluoride was formed.

Group V. Nitrogen: The nitrogen atom in its compounds forms quite a few coordination compounds with BF_3. These may be of the type:

$N.BF_3$, where N is ammonia (1)(27)(34)(70), trimethyl amine (17)(23)(65), triethyl amine (46), diethyl amine (46), ethylamine (46), acetamide (16), aniline (50)(79)(84), dimethylaniline (17)(69)(84), acetanilide(84), methyl acetanilide(84), monosodium- and monopotassium-aniline (64), benzalaniline (81), p-aminobenzoic acid (83), acetophenone oxime (41), p-tolylphenyl ketoxime (41), pyridine (21)(87), quinoline (16), piperidine (16).

$2N.BF_3$, where N is ammonia (27)(34)(79)
$3N.BF_3$ where N is ammonia (27)(79)
$N.2BF_3$ where N is pyridine (16) and brucine (50)
$N.4BF_3$ where N is hexamethylenetetramine (91)
$RCN.BF_3$ where R is H, CH_3, C_6H_5, $H_3C-C_6H_4$ (76)
N_2O is unreactive with BF_3 at low temperatures (13).

Phosphorus. Only phosphine has been reported to donate to BF_3, forming the compounds $H_3P.BF_3$ (89) and $H_3P.2BF_3$ (10)(89).

Group VI. Oxygen-inorganic. Oxygen in inorganic compounds seems to be a better donor when it is not attached to another atom by a double bond. The types of compounds reported are:

$HOH.BF_3$ (63)(68)(86); $H_2O.BF_3.2C_{10}H_{18}O$ and $H_2O.BF_3.C_4H_8O_2$ (63)(68)
$2HOH.BF_3$ (2)(3)(4)(9)(33)(35)(51)(60)(63)(68)(92); dihydroxyfluoboric acid $H_2O.BF_2.OH$ (48); $2H_2O.BF_3.2C_{10}H_{18}O$ and $2H_2O.BF_3.C_4H_8O_2$ (63)(68)

BF_3

$3HOH.BF_3$ (59)
$MOH.BF_3$ where M = Na or K (60), Ca, H_2PO_3 or $H_3P_2O_6$ (45)
$MO.BF_3$ where M = Ca (29), B_2O_2 (5)(80), P_2O_4 (37)(40)
$M_2O.4BF_3$ where M = alkali metal or NH_4 (85)
$M_2SO_4.BF_3$ where M = Na, K, Tl, ($Cs.2BF_3$) (6)(7)
$Na_3PO_4.3BF_3$, $K_3PO_4.3BF_3$, $Na_4P_2O_7.4BF_3$, $K_4P_2O_7.4BF_3$ (6)
$NaOCH_3.BF_3$, $KOCH_3.BF_3$ (68), $Hg(OCH_3.BF_3)_2$ (75)
$POF_3.BF_3$ (14); $POCl_3$, SO_2Cl_2 do not react (22)
See table III.

Oxygen-organic. As early as 1878 Landolph (56) reported that BF_3 combines "equivalent for equivalent with aldehydes, ketones and carbonyls." Gasselin (33) in 1894 observed that the presence of oxygen in an organic molecule is a favorable condition for coordination with BF_3. As will be shown below, an oxygen attached by a double bond does not coordinate with BF_3 as easily as an oxygen atom attached to two other atoms by single bonds.

Alcohols. Two series of compounds have been reported as formed by BF_3 and alcohols. They are:

$ROH.BF_3$ where R = CH_3 (33)(75)(88), C_2H_5 (16)(33), i-C_4H_9 (29) glycol (33)(68), C_6H_5 (82).
$2ROH.BF_3$ where R = CH_3, C_2H_5, n-C_3H_7, sec-C_3H_7, n-C_4H_9 (63)(68) CH_2ClCH_2, CCl_3CH_2 (68), $C_6H_5CH_2$ (24)(68), C_6H_5 (33) (68)

Meerwein and Pannwitz (68) concluded that the stability of BF_3-alcohol complexes is decreased if a polar or easily polarisable group, e.g. CH_2Cl, CCl_3, or C_6H_5, is in the immediate proximity of the hydroxyl group. See Table IV.

Aldehydes. Very few coordination compounds of BF_3 with aldehydes have been reported.

$RCHO.BF_3$ where R = CH_3, $(CH_3)_3C$, Cl_3C (20)

Valenic and benzyl aldehydes have been reported to react equivalent for equivalent with BF_3 (52)(55)(56).

Ketones. Only acetone (33) and benzoyl acetone (69) have been reported to form one to one coordination compounds with BF_3. BF_3 has been reported to react with acetone (20)(33)(50)(56)(57), methyl nonyl ketone, camphor (52)(53)(56) and benzoyl acetone (73).

Acids. Analogous to the alcohol compounds, we find two series of acid compounds with BF_3, namely:

$RCOOH.BF_3$ where R = H (68), CH_3 (43)(62)(63)(68), C_2H_5 (16)(68) n-C_3H_7 (68), $H_3CCH = CH$ (68), COOH (68), $COOH(CH)_2$ (68), $COOH(CH_2)_2$ (68), C_6H_5 (16)(68), $C_6H_5CH_2$ (68)

$2RCOOH.BF_3$ where R = H (68), CH_3 (16)(44)(63)(64)(68), CH_2Cl (16)(63)(68), C_2H_5 (68), n-C_3H_7 (68), i-C_3H_7 (69), $H_3CCH = CH$ (68),

Meerwein and Pannwitz draw the same conclusion about the stability of acid-BF_3 compounds that they did about alcohol-BF_3 compounds. Groxall, Sowa, and Nieuwland conclude that there is a greater tendency for BF_3 to coordinate with the carboxy or carbalkoxy groups than with the phenolic group (25). See Table V.

Ethers. The ether compounds with BF_3 are fairly well known. Those that have been reported are one to one compounds with methyl (18)(19)(31)(33)(38)(57a), ethyl (31)(33)(57a)(74)(90), methyl ethyl (57a)(66) methyl i-propyl (68), methyl amyl (67), n-propyl (65), i-propyl (18)(74), i-propyl phenyl (74), amyl (74), i-amyl (74), dibenzyl (74), ethyl benzyl (74), ethyl phenyl (16)(67), methyl phenyl (16)(67) ethers. Attempts with diphenyl ether have failed (16)(67). See Table VI.

$BF_3.2(n\text{-}C_3H_7)_2O$ has been reported by Meerwein and Pannwitz (68). Other miscellaneous compounds of the ether type are $C_4H_8O.BF_3$ (18) and the betaines produced by the reaction of BF_3 complexes with ethylene oxide or epichlorohydrin (65).

Acid anhydrides. $BF_3.O(CH_3CO)_2$ was reported in the same month in 1931 by Bowlus and Nieuwland (16) and by Morgan and Taylor (71). Two years later Meerwein (63) refuted their work and said the compound was $[(CH_3CO)_2CHCO]_2O.BF_3$. Similarly, he reported propionic, n-butyric, and i-butyric anhydrides to form compounds of the type $(RCOCHRCO)_2O.3BF_3$. Later with i-butyric anhydride he reported $[i\text{-}C_3H_7CO.C(CH_3)_2.CO]_2O.3BF_3$, and with chloracetic and phenylacetic anhydrides, molecular compounds (69). With succinic, benzoic, and phthalic anhydrides Bowlus and Nieuwland (16) obtained no reaction, however $BF_3.O(H_2CCO)_2$ has since been reported (67).

Esters. Esters have been found to form stable coordination compounds with BF_3. The Notre Dame workers, studying the mechanism of the alkylation of benzene using BF_3 as a catalyst, have postulated the formation of an intermediate complex of an ester with BF_3 (26)(61). As a result, many BF_3-ester compounds have been postulated, but comparatively few isolated. Those isolated and reported are:

$CH_3.OCOR.BF_3$ where R = H (71), CH_3 (16)(71), CH_2OH (72), C_6H_5(72).
$C_2H_5.OCOR.BF_3$ where R = H (16)(71), CH_3 (16)(71), C_2H_5 (16).
$C_3H_7OCOCH_3.BF_3$ (16)

The following compounds absorbed one mole of BF_3 to form viscous liquids or crystalline compounds but existance of molecular compounds was not established: ethyl chloroacetate, ethyl trichloroacetate, ethyl benzoate, diethyl oxalate, diethyl malonate, diglycol acetate, phenyl acetate (16) and p-tolyl acetate (41)

Sulfur-inorganic: Sulfur in compounds such as H_2O (37), SO_2 (13), SOF_2 (14), has been found to be a donor to the boron atom of BF_3 forming one to one molecular compounds. See Table III. However, in compounds such as $SOCl_2$ (22) and PSF_3 (14) the sulfur atom did not donate

Group VII, Fluorine. Booth and Carter (12) suggest that BF_3 is associated at a pressure around 10 atmospheres, which could only come about by $BF_2F \longrightarrow BF_3$. Berzelius (8) passed BF_3 into water and produced fluoboric acid, which can be written $HF.BF_3$. Landolph reported "hydroboric fluoride" which can be written $BF_3.3HF$ (54). More recently $BF_3.2HF$ has been reported (42).

Compounds of the type $MF_2.BF_3$ and $MF_2.2BF_3$ where M = Fe or Co have been reported (58). $2CaF_2.BF_3$ has also been isolated (39). The alkali metal fluorides form compounds $MF.BF_3$ (28)

Other miscellaneous compounds are $NOF.BF_3$ and $CH_3CO^+BF_4^-$. The chlorofluorides of methane have limited miscibility in BF_3.

Chlorine. A du Pont patent (29) claims that organic coordination compounds with BF_3 are released from the BF_3 by the addition of a halide of Na, Zn, Al, Cu, Pb, Fe, or Sn. The inorganic halide coordinates with the BF_3 and thus releases the organic compound. NaCl was an example cited.

HCl and CH_3 do not react with BF_3 (13)(38).

Group VIII. No compounds with elements in this group as donors have been reported.

Summary. The elements which in their compounds are donors to the boron atom of BF_3 are in a small area of the non-metallic part of the Periodic Table, thus

C N O F
P S Cl A.

TABLE	COMPOUND	MELTING POINT °C	BOILING POINT °C	REFERENCE
I	$A.BF_3$	-128.6		15
	$A.2BF_3$	-127.3		
	$A.3BF_3$	-128.3		
	$A.6BF_3$	-128.3		
	$A.8BF_3$	-128.4		
	$A.16BF_3$	-129.0		
II	$NH_3.BF_3$	180		46
	$C_2H_5NH_2.BF_3$	89		46
	$(C_2H_5)_2NH.BF_3$	160		46
	$(C_2H_5)_3N.BF_3$	29.5	80_3	46
	$(C_6H_5)(CH_3CO)HN.BF_3$	135		84
	$(C_6H_5)(CH_3CO)CH_3N.BF_3$	114		84
	$C_6H_5CH{:}NC_6H_5.BF_3$	135-45		81
	$C_6H_5(CNOH)CH_3.BF_3$	107-13		41
	$C_5H_5N.BF_3$	45	300	2187
	$HCN.BF_3$	40		76
	$CH_3CN.BF_3$	87	$100_{.752}$	16
III	<u>oxygen:</u>			
	$H_2O.BF_3$	5.4-6		63 68
	$2H_2O.BF_3$	4.6-5	$58.5-60_{1.2}$; $46_{4.6-5}$	63 68
	$C_4H_3O_2.H_2O.BF_3$	128-30 (decomp.)		68
	$C_4H_3O_2.2H_2O.BF_3$	142		63 68
	$2C_{10}H_{18}O.H_2O.BF_3$	71-3		68
	$2C_{10}H_{18}O.2H_2O.BF_3$	59.5-61		63 68
	<u>Sulfur</u>			
	$H_2S.BF_3$	-137.0		37
	$SO_2.BF_3$	- 96.0		13
	$SOF_2.BF_3$	-140.8		14
IV	$CH_3OH.BF_3$	-19.4		75
	$C_2H_5OH.BF_3$	-19		16
	$(CH_2OH)_2.BF_3$	40-4		63, 68
	Dialcoholates			
	$2CH_3OH.BF_3$		58.9_4	63, 68
	$2C_2H_5OH.BF_3$		60_4; $51-2_{15}$	63, 68
	$2C_3H_7OH.BF_3$		56_2	63, 68
	$2C_4H\ OH.BF_3$		$64.5-70_3$	63, 68
	$2CH_2ClCH_2OH.BF_3$		$59_{2-2.5}$	63, 68
	$2CCl_3CH_2OH.BF_3$	40-2		68
V	$HCOOH.BF_3$	-20-1		68
	$CH_3COOH.BF_3$	-23-4	59_{13}; 62_{11}	62,68,69
	$C_2H_5COOH.BF_3$	-28-9		68
	$n-C_3H_7COOH.BF_3$	-29-30		68
	$CH_3CH{:}CHCOOH.BF_3$	-55-6		68
	$C_6H_5COOH.BF_3$	+90-1.5(decomp) (98 crude)		16, 68
	$C_6H_5CH_2COOH.BF_3$	+56-9(decomp)		68

TABLE	COMPOUND	MELTING POINT °C	BOILING POINT °C	REFERENCE
V (cont.)	$2HCOOH.BF_3$		$43-4_{11}$	68
	$2CH_3COOH.BF_3$		$53-4_{18}$; 140_{746}; 142	16, 68
	$2C_6H_5COOH.BF_3$		$60-60.5_{12}$; $62-3_{17}$	16, 68
	$2n-C_3H_7COOH.BF_3$		84_{11}	68
	$2i-C_3H_7COOH.BF_3$		$68-70_{15}$	69
	$2CH_3CH:CHCOOH.BF_3$		$81-2_{12.5}$	68
	$(COOH)_2.BF_3$	57-8(decomp.)		68
	$(CHCOOH)_2.BF_3$	75-82		68
	$(CH_2COOH)_2.BF_3$	84-4(decomp.)		68
VI	$(CH_3)_2O.BF_3$	-10-4	126-8	18,31,38 57a
	$(C_2H_5)_2O.BF_3$	-50-2;-60.4	123-5.7	18, 57a
	$(i-C_3H_7)_2O.BF_3$	68		18
	$(CH_3)(C_2H_5)O.BF_3$	-98	127	57a
	$(CH_3)(C_5H_{11})O.BF_3$	-41	$54.8-5_{10}$	67
	$(CH_3)(C_6H_5)O.BF_3$	-12-3		67
VII	$C_2H_5O_2CCH.BF_3$		102_{748}	16
	$CH_3O_2CCH_3.BF_3$	60	110_{739}	16
	$CH_3O_2CCH_2OH.BF_3$		60_3	72
	$C_2H_5O_2CCH_3.BF_3$	26	119_{739}	16
	$C_3H_7O_2CCH_3.BF_3$		126_{743}	16
	$C_6H_5O_2CCH_3.BF_3$	40-55		72
	$p-CH_3.C_6H_4O_2CCH_3.BF_3$	146-50		41
	$C_2H_5O_2CC_2H_5.BF_3$	33	116_{747}	16

BIBLIOGRAPHY

1. Balz and Zinser, Z. anorg. allgem. Chem., 221, 225-48 (1935)
2. Basarow, Ber., 7, 823 (1874)
3. -------, Bull. soc. chim., [2] 21, 290 (1874)
4. -------, Compt. rend., 78, 1698-1700 (1874)
5. Baumgarten and Bruns, Ber., 72B, 1753 (1939)
6. ---------- and Hennig, ibid, 72B, 1743 (1939)
7. ---------- and Müller, ibid, 69B, 2688-90 (1936)
8. Berzelius, Pogg. Ann., 2, 113 (1824)
9. ---------, ibid, 58, 503 (1843)
10. Besson, Compt. rend., 110, 80 (1890)
11. Booth, H. S., Private Communication.
12. ----------, and Carter, J. Phys. Chem., 36, 1359 (1932)
13. ----------, and Martin, D. R., J. Am. Chem. Soc., 64, 2198-2205 (1942)
14. ----------, and Walkup , J. R., ibid, 65, 2334-39 (1943)
15. ----------, and Willson, K. S., ibid, 57, 2273-80 (1935)
16. Bowlus and Nieuwland, ibid, 53, 3835 (1931)
17. Bright, J. R. and Fernelius, W. C., ibid, 65, 735-6 (1943)
18. Brown H. C., and Adams, ibid, 64, 2559 (1942)
19. ---------- and Adams, R. M., ibid, 65, 2253-4 (1943)
20. ----------, Schlesinger and Burg, ibid, 61, 673 (1939)
21. ----------, ----------, and Cardon, ibid, 64, 325 (1942)

22. Burg, A. B. and Ross, M. K., ibid, 65, 1637-8 (1943)
23. ---------- and Sister Agnes A. Green, ibid., 65, 1838-41 (1943)
24. Cannizzaro, Ann., 92, 113 (1854)
25. Croxall, Sowa, and Nieuwland, J. Am. Chem. Soc., 56, 2054 (1934)
26. -------, ----, and ---------, J. Org. Chem., 2, 253 (1937)
27. Davy, J., Phil. Trans., 102, 352 (1812)
28. de Boer and van Liempt, Rec. Trav. Chim., 46, 124 (1927)
29. E. I. du Pont de Nemours and Co., Inc., Brit. 486, 887, June 13, 1938.
30. Gasselin, Bull. soc. chim., (3)7, 17-18 (1892)
31. -------, ibid., (3)7, 209 (1892)
32. -------, ibid., (3)9, 401 (1892)
33. -------, Ann. chim. phys., (7)3, 5 (1894)
34. Gay Lussac, Gilbert Ann., 36, 6 (1810)
35. ---------- and Thenard, Recherches physico-chimiques, 2, 38 (1811)
36. Gerhart and Hull, (to Standard Oil Co. of Indiana) U.S. 2, 148, 115 Feb. 21, 1939; French 823, 270 Jan. 18, 1938.
37. German, A. F. O. and Booth, H. S., J. Phys. Chem., 30, 369 (1926)
38. ---------- and Cleveland, M., Sci., 53, 582 (1921)
39. ---------- and Torrey, G. G., ibid, 54, 16 (1921)
40. Goring, Helen W., "Reactions of Boron Trifluoride", M. S. Thesis, Western Reserve University, Cleveland, Ohio (1927)
41. Grumitt, M. S. Thesis, Western Reserve University, Cleveland, Ohio.
42. Hantzsch, Ber., 63, 1789 (1930)
43. Hardtman, Tietze, and Schepss, (to I. G. Farbenindustrie A. G.) Ger. 551, 513 October 18, 1927.
44. Hinton and Nieuwland, J. Am. Chem. Soc., 54, 2017 (1932)
45. I. G. Farbenindustrie A. G., Brit. 451, 359 Aug. 4. 1936.
46. Kraus and Brown, J. Am. Chem. Soc, 51, 2690 (1929)
47. Krause and Knobbe, Ber., 64B, 2112 (1931)
48. Kroeger, Sowa, and Nieuwland, J. Am. Chem. Soc., 59, 965 (1937)
49. Kuhlman, Ann. chim. phys., (3)2, 116 (1841); Liebig's Ann., 39, 319, (1841)
50. Landolph, Ber., 12, 1578 (1879)
51. --------, ibid., 12, 1583 (1879)
52. ---------, Compt. rend., 85, 39 (1877)
53. ---------, ibid, 86, 539 (1878)
54. ---------, ibid, 86, 601 (1878)
55. ---------, ibid, 86, 671 (1878)
56. ---------, ibid, 86, 1463 (1878)
57. ---------, ibid, 89, 173 (1879)
57a. Laubengayer and Finlay, J. Am. Chem. Soc., 65, 884-9 (1943)
58. Long, K. E., M. S. Thesis, Western Reserve University (1927)
59. McAlevy, (to E. I. du Pont de Nemours and Company, Inc.,) U. S. 2, 135, 454, November 1, 1938.
60. McGrath, J. S., Stack, G. G., and McCusker, P. A., J. Am. Chem. Soc., 66, 1263-4 (1944)
61. McKenna and Sowa, ibid., 59, 1204 (1937)
62. Meerwein, Ann., 455, 227 (1927)
63. --------, Ber., 66B, 411 (1933)
64. --------, Sitzber, Ges. Beforder. ges. Naturw. Marburg, 64, 119 (1930); Chem. Zentr., 2, 1962 (1930)
65. --------, Battenberg, Gold, Pfeil, and Willfarg, J. prakt. Chem., 154, 83 (1939)

66. ---------, Hinz, Hofmann, Kronig and Pfeil, ibid., 147, 257 (1937)
67. ---------, and Maier-Hüser, ibid, 134, 51 (1932)
68. ---------, and Pannwitz, ibid, 141, 123 (1934)
69. --------- and Vossen, ibid, 141, 149 (1934)
70. Mixter, Am. Chem. J., 2, 153 (1880)
71. Morgan and Taylor, J. Soc. Chem. Ind., 50, 869 (1931)
72. ------ and ------, J. Chem. Soc., (1932), 1497
73. ------ and Tunstall, ibid., 125, 1963 (1924)
74. O'Connor and Sowa, J. Am. Chem. Soc., 60, 125 (1938)
75. O'Leary and Wenzke, ibid., 55, 2117 (1933)
76. Pattein, Compt. rend., 113, 85 (1891)
77. Price and Ciskowski, J. Am. Chem. Soc., 60, 2499 (1938)
78. ----- and Meister, ibid., 61, 1595 (1935)
79. Rideal, Ber., 22, 992 (1889)
80. Ruff, Braida, Bretschneider, Menzel and Plant, Z. anorg. allgem. Chem., 206, 59 (1932)
81. Snyder, Kornberg, and Romig, J. Am. Chem. Soc., 61, 3556 (1939)
82. Sowa, Hinton and Nieuwland, ibid., 55, 3402 (1933)
83. ---- and Nieuwland, ibid., 58, 271 (1936)
84. Sugden, S. and Waloff, M., J. Chem. Soc., (1932), 1492
85. Swinehart (to Harshaw Chemical Company) U.S. 2, 148, 514 February 28, 1939; U.S. 2, 196, 907 April 9, 1940.
86. Thomas, Anzilotti, and Hennion, Ind. Eng. Chem., 32, 408 (1940)
87. van der Meulen and Heller, J. Am. Chem. Soc., 54, 4404 (1932)
88. Vaughn, Bowlus, and Nieuwland, Proc. Indiana Acad. Sci., 40, 203-6 (1931)
89. Wiberg and Heubaum, Z. anorg. allgem. Chem., 225, 270 (1935)
90. ------ and Mathing, Ber., 70B, 690-7 (1937)
91. Burg, A. B. and Martin, L. L., J. Am. Chem. Soc., 65, 1635-7 (1943)
92. Klinkenberg and Ketelaar, R. . trav. chim., 54, 959 (1935)

ROLL CALL

December 12, 1944

luminum Phosphide — T. G. Klose

The literature reports five binary compounds of phosphorus and luminum -- Al_3P_5, Al_3P_7, Al_5P_3, Al_3P and AlP. Since the analyses of ome of these compounds are unrecorded or questionable, an attempt as made to find the correct composition of aluminum phosphide(s).

Various preparative methods are given, the most successful one eingthe process in which a mixture of finely divided aluminum and nosphorus is heated in an atmosphere of phosphorus vapor.

A complete analysis of the product is given. This analysis is esigned to calculate phosphide phosphorus, free aluminum, total luminum and phosphorus pentoxide.

X-ray diffraction studies of the phosphide preparations were made o determine the free aluminum concentrations in the various samples. he results were in agreement with chemical analysis. X-ray studies lso indicated that the chief constituent was AlP and was identical or all preparations regardless of the amount of free aluminum present.

Aluminum phosphide is dark-gray to yellowish-gray in color. It oesn't decompose at temperatures as high as 1000°C. It is easily ydrolyzed by acids, bases, or water, one of the products of the re-ction being phosphine.

eference:
hite, W. E. and Bushey, A. H., J.A.C.S 66, 1666 (1944)

---

reparation of Potassium Chloroplatinite — James V. Quagliano

Yellow, insoluble potassium chloroplatinate is prepared by the eaction of solutions of chloroplatinic acid and potassium chloride:

$$H_2PtCl_6.6H_2O + 2KCl \longrightarrow K_2PtCl_6 + 2KCl + 6H_2O$$

he K_2PtCl_6 is suspended in water and reduced with freshly prepared O_2-water. The vessel is placed on a steam bath and during the reduc-ion process the solution is stirred constantly with a mechanical tirrer. Tetravalent platinum is reduced to the divalent state ccording to the following equation:

$$PtCl_6^{=} + SO_2 + 2H_2O \longrightarrow PtCl_4^{=} + SO_4^{=} + 2Cl^- + 4H^+$$

he "temperature of a steam bath" is indefinite and to insure complete eduction it is necessary to state the temperature range (85-90°C) o which the solution must be heated.

Tech Info

November 12, 1919

Electron Plasticity — T. G. Kline

The literature reports five binary compounds of aluminum and — Al_4Be_3, Al_2Be_3, $AlBe_2$, $AlBe_3$ and $AlBe_5$. Since the melting points of these compounds are extremely or sensitivity, an effort was made to find the eutectic composition of minimum composition.

Various properties including the most successful cold electrode process in which a mixture of finely divided aluminum and beryllium is heated in an atmosphere of phosphorus vapor.

A complete analysis of the product is given. This analysis is employed to calculate physical properties, from elasticity, tensile strength and physical-form variations.

X-ray diffraction studies of the composite specimens were made to determine the free aluminum content existing in the various samples. The results were in agreement with chemical analysis. X-ray studies also indicated that the coarse particulate was AlBe and was identical with all preparations regardless of the amount of free aluminum present.

Aluminum possesses in Zone-Level to yellowish-green in color. It is insoluble at temperatures up to 1000°C. It is easily attacked by acids, bases, or water, and the products of the reaction are hydrogen.

References

Ritz, T. and Sauer, R. G., J.A.C.S. 66 1082 (1944)

Preparation of Titanium Chlorohydrate — James K. Sampson

Titanium chlorohydrate production apparatus is prepared by the reaction of titanium (V) chlorohydrate with potassium chlorate

$$TiCl_4 \cdot 6H_2O + KClO_3 \longrightarrow TiCl_4 \cdot 5H_2O + KCl$$

The titania is separated in water and reduced with freshly prepared hydrogen. The vessel is placed in a place such and during the reaction process. The reaction is carried out in a mechanical stirrer. Temperature control is reduced to the minimum while according to the following equation:

$$TiCl_4 \cdot 5H_2O + 2H_2O \longrightarrow TiCl_4 \cdot 7H_2O + KCl + 4H^+$$

The "temperature of a clean batch" is determined and is usually required if it is necessary to which the temperature range (60-80°C) within the activities must be tested.

mphiprotic Substances Elizabeth W. Peel

Basic substances are proton acceptors (electron donors); acidic ubstances are proton donors (electron acceptrs). The former are xemplified by ammonia and amines, the latter by acids. Acetamide CH_3CONH_2) in water solution is essentially neutral, since it will either accept a proton from H_3O^+ nor donate one to OH^-, which ions re the strongest acid and base possible in water solution. In other olvents, however, it has been shown to possess both acid and basic roperties. For instance, in glacial acetic acid solution, acetamide an be titrated with perchloric acid, the potentiometric curve showing t to be a weak base in this case. Also, in liquid ammonia, it will eact with sodamide to give a sodium derivative, donating a proton to he NH_2^- ion, thus acting as an acid.

The authors of this article have investigated further the be-avior of acetamide in these solvents, determining the freezing point urves for the systems CH_3CONH_2-CH_3COOH (1), and CH_3CONH_2-NH_3(2). In ach case, they found definite evidence for a 1:1 compound between the wo components.

In case (1), the compound melts incongruently, decomposing just elow its melting point (about 6°C), so the curve shows a break, no aximum, at slightly more than 50 mole percent acetic acid. The com-ound was isolated and analyzed acidimetrically; it corresponds to he following:

$$CH_3CONH_2 + HC_2H_3O_2 \rightleftharpoons (CH_3CONH_3)^+ (C_2H_3O_2)^-$$

nd may be called acetylammonium acetate.

In case (2), the compound decomposes well below its melting point, he break in the curve coming at about 70 mole percent ammonia. The ompound was not isolated, since it is so unstable. It would cor-espond to:

$$CH_3CONH_2 + NH_3 \rightleftharpoons (CH_3CONH)^-(NH_4)^+$$

nd may be called ammonium aquo-ammono-acetate.

Acetamide has thus been shown to be definitely amphiprotic.

eference:
isler, Davidson, Stoenner and Lyon, J. Am. Chem. Soc. 66, 1888 (1944)

Bibliography

Dirichlet, G. Lejeune

Dirichlet integrals are proven analytic functions (Lichtenstein assertion) exists [illegible] are proven analytic (Lichtenstein assertion). The former are [illegible] by Jeans, and Wolfram, the latter by Picard. Analytic [illegible] in water solution is questionably valuable, since it will [illegible] from the [illegible] in water solution. To [illegible] however, it has been shown to contain both real and imaginary [illegible]. For instance, in glacial cobalt only [illegible] is filtered with questionable art, the potentiometric [illegible] to be a weak base in this case. Also, in liquid ammonia, it will react with acetonitrile to give a sodium derivative, acetylene a [illegible] "ic" ion, from which is an acid.

The [illegible] of this article have investigated fluorine and the [illegible] of acetylene in these solvents, determining the freezing point curves for the systems [illegible] (1), and [illegible] (2). In [illegible] way, they found artificial evidence for a 1:1 compound [illegible] in chlorobenzene.

In case (1), the [illegible] melts congruently, [illegible] [illegible] the melting point (about 0°C), so the curve [illegible] a [illegible] minimum, at slightly over [illegible] mol % [illegible] mixture. The [illegible] was treated and compared mathematically to [illegible] the following:

$$[illegible] = [illegible] \exp\left(\frac{[illegible]}{[illegible]}\right)$$

[illegible] for the ideal [illegible] solution [illegible].

In case (2), the compound decomposes well below its melting point [illegible] in the curve leading at about 70 mole percent acetylene. The [illegible] and are not isolated, since it is so unstable. It could [illegible] [illegible] by:

$$[illegible] \rightleftharpoons [illegible] \exp\left(\frac{[illegible]}{[illegible]}\right)$$

[illegible] for an ideal [illegible] equilibrium-constant.

Unknown was [illegible] which is a definitely [illegible].

Elements:

[illegible] Brittain, Shakeshaft (A) [illegible], J. Am. Chem. Soc., [illegible] (1964)

Molecular Compounds Between Amines and Sulfur Dioxide. Comments on Jander's Theory of Ionic Reactions in Liquid Sulfur Dioxide.

A. L. Oppegard

The authors claim that Jander's theory is based on experimental work which is not reliable. Errors were made in analyses, and molecular weight determinations were not made. The authors repeated Jander's work, but with vastly different results.

Jander's work and interpretation.

$$(C_2H_5)_3N \xrightarrow[SO_2]{liq.} \left[\begin{matrix}(C_2H_5)_3N \\ (C_2H_5)_3N\end{matrix}\!\!>SO\right] SO_3 \xrightarrow{KBr} \left[\begin{matrix}(C_2H_5)_3N \\ (C_2H_5)_3N\end{matrix}\!\!>SO\right] Br_2$$

Colorless, crystalline m.p. 73°C. I

m.p. 230°C. II

This article

$$(C_2H_5)_3N \xrightarrow[SO_2]{liq.} (C_2H_5)_3N{:}SO_2 \xrightarrow{H_2O} (C_2H_5)_3NH(HSO_3) \xrightarrow{O_2} (C_2H_5)_3NH(HSO_4)$$

orange oil mol. wt. det'd III

Colorless crystalline m.p. 74-75°C. IV

m.p. >115°C. V

It is pointed out that I and IV are probably the same compound and also that II was probably $(C_2H_5)_3N.HBr$ (m.p. 248°C) plus some IV.

Previous work on the reactions between amines and liquid sulfur dioxide indicates that they combine in a 1-1 ratio to give a simple molecular compound $R_3N \longrightarrow SO_2$.

On the basis of their work the authors conclude that reactions between amines and liquid sulfur dioxide are merely addition reactions and not ionic, as Jander states.

The exact structure of III puzzled the writers. The structure shown does not explain the intense color, nor the slight conductivity exhibited in liquid sulfur dioxide.

Reference.

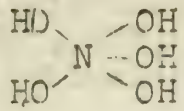
L. C. Bateman, E. D. Hughes, C. K. Ingold, J. Chem. Soc. 243 (1944)

For a review of Jander's theory see Emeleus and Anderson, Modern Aspects of Inorganic Chemistry, page 482.

The Structure of Orthonitric Acid

Hans B. Jonassen

When dry air is passed through a solution of dilute nitric acid at -15°C. needle-like crystals are obtained which have a composition corresponding to $HNO_3.2H_2O$. Erdmann (1)(2) and Mellor (3) assigned the following structure to this "compound":

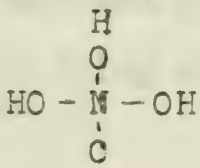


This compound is unstable above -15°C.

Küster and Krumann (4) however, reporting on the thermal analysis of the system H_2O and HNO_3, obtained data indicating that no definite compound is formed at a position corresponding to a composition $HNO_3.2H_2O$. Their data only indicate the existence of the compounds $HNO_3.H_2O$ and $HNO_3.3H_2O$.

If, however, a mixture of acetic anhydride and nitric acid is distilled and the fraction boiling at 127°C is collected, analysis shows that the composition of this fraction corresponds to a compound $(CH_3COOH)_2.HNO_3$. This compound is called "Diacetyl Orthonitric" acid (2). It is unstable in the presence of water, giving acetic acid and nitric acid.

Biltz, reporting on his investigation of the system HNO_3 and H_2O, states that the compound $HNO_3.H_2O$ should be called ortho nitric acid. He assigned to it the following structure corresponding to the structure of orthophosphoric acid:



Zintl and Haucke (6) report in 1935 that they were able to isolate Na_3NO_4 and that they subjected this compound to x-ray investigations. These investigations seem to prove that during the formation of this compound from Na_2O and $NaNO_3$ the oxygen atom of the Na_2O is able to push aside the third oxygen atom of the nitrate ion to form the NO_4^{-3} ion which then acts as the central group of the compound. This compound is stable although the coordination number of nitrogen derived from the ratio of radius of cation/radius of anion gives a coordination number of three for nitrogen.

Zintl, Morawitz, and Waltersdorf (7) investigated also the orthonitric acid proposed by Biltz (5) by means of x-ray at -150°C, and at -80°C. They state that their data seem to indicate the same structure proposed by Biltz (5) for the orthonitric acid, because the x-ray pattern of this compound was somewhat

The Structures of Methylcitric Acid Peter E. Newren

When dry air is passed through a solution of citric acid with at -15°C, needle-like crystals are obtained which have a composition corresponding to $C_7H_8O_7$. Thomas [3][4] has noted that the melting and following structure to this "compound"

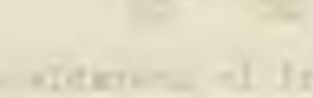
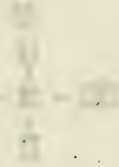


Table 1. Compound I: melting-point -15°C.

Under the Crossen [1] system, methylcitric acid is formed in the reaction of the acetone C_7 and C_8, yielding the intermediate $C_8H_8O_7$ (Figure 1). In formed at a quantity corresponding to a compound of $C_{8.5}H_{8.5}O_7$. This data only indicate the existence of the compound $C_8H_8O_7$ and $(C_7H_8O_7)_2$.

It, however, a mixture of equal molecular and nitric acid is distilled and the fraction boiling at 127°C is collected, analysis shows that the composition of the fraction corresponds to a compound $(C_8H_{10}O_7)_2$. This compound is called "citromethylic acid" [2]. It is obtained by the presence of water, giving methylcitric acid and citric acid.

Pitts, recording an old hypothesis of the system CO_2, and H_2O, stated that the compound $(C_8H_{10}O_7)_2$ should be called methylcitric acid. He designed it by the following structure corresponding to the structure of citric compound acid:

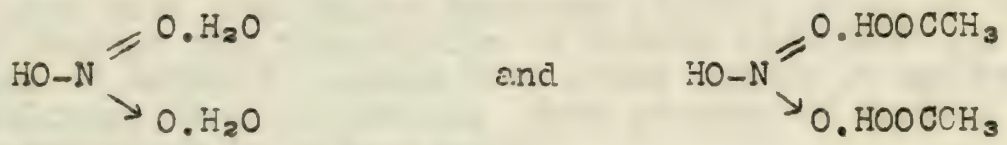


Since Mr. Brooks [5] found in 1928 that they were able to isolate $C_8H_{10}O_7$, and that was obtained this compound in a-ring constituent. Since investigations were by which this method the formation of this compound from lime and H_2SO_4, the action of the CO_2 is able to give citric the lime oxygen atom of the nitric. In a fact, the $C_8H_{10}O_7$ has which as the central group of the compound. This compound is above already the condition, if citromethylic having the meta or ortho of nitrocitric or meta group a acetylation method of this for citric.

Since, Brooks and Whitmore [6] investigated also the structure of citromethylic acid. Is with $C_8H_{10}O_7$ the ratio of weight of -ylic, -ron, -ol, -ic. The ether in a similar data was to isolate the structure compound of this [6] for the orthocitric acid, neither the -ons active of a the acetone and acetone.

similar to that of the Na_3NO_4. They state, however, that the similarity is not outspoken enough to definitely prove this structure.

The "orthonitric" acid $HNO_3.2H_2O$ isolated by Erdmann (1)(2) and the related $HNO_3.2CH_3COOH$ seem only to be dipolar association compounds of the following structure:



This dipolar association seems to be substantiated by the following facts:

(1) "Diacetyl orthonitric" acid is unstable in the presence of water, forming acetic acid and nitric acid.

(2) This instability can be explained if dipolar association is assumed because in the case of such a linkage a group with a higher dipole moment may be assumed to displace one which has a lower dipole moment. The dipole moment of H_2O is 1.80 Debye units whereas that of CH_3COOH is 1.72 Debye units.

(3) Küster and Krumann were unable to show the presence of a compound corresponding to the composition $HNO_3.2H_2O$ in their thermal analysis data.

(4) Constant boiling nitric acid has the composition $HNO_3.2H_2O$.

Bibliography

1. Erdmann, Z. anorg. Chem. 32, 431, (1902), 34, 131 (1903).

2. Erdmann, Z. angew. Chem. 16, 1079 (1903).

3. Mellor, Comprehensive Treatise of Inorg. Chem., Vol. VIII, p. 564.

4. Küster and Krumann, Z. anorg. Chem. 41, 1, (1904)

5. Biltz, W. Nachr. Ges. Wiss. Gottingen. Math. Phys. Kl. (N. F.) 1, 95 (1935).

6. Zintl and Haucke, Z. phys. Chem. A174, 314, (1935).

7. Zintl , Morawitz, and Waltersdorf, Naturw. 23, 197 (1935).

similar to that of the SO_4^{2-}. This suggests, however, that the electricity is not responsible enough to definitely prove this conjecture.

The "dehydrated" acid $HO_3As_2O_5$ isolated by Sommer (1)(c) and the mixture $HO_3As_2O_5 \cdot 3H_2O$ were only to be dibasic neutralized corresponds to the following structure:

This simpler substitution series is substantiated by the following facts:

(1) "Diarsyl arsenoxide" acid is insoluble in the presence of water, forming acetic acid and dirty white.

(2) This insolubility can be utilized to distinguish monobasic pyrosulfate in the case of well a liquid a prep with a higher dibasic acid, can be measured to identifica tion which has a lower dibasic acid. The dibasic acid of $HO_3As_2O_5$ is 1.7% higher acid.

(3) Kahler and Krauss were unable to show the presence of a compound corresponding to the composition HO_3As_2O in their thermal analysis data.

(4) Lumsden boiling dibasic acid; has the composition $HO_3As_2O_5$.

Bibliography

1. Sommer, E. Monats Chem. 28, 431, (1907); 29, 121 (1908).
2. Erdmann, H. Ferr. Chem. 36, 1377 (1903).
3. Fuller, Crystallography Publication of Chem. Soc., 7a, 1921; 2, 104.
4. Kahler and Krauss, Z. anorg. Chem. 41, 1, (1904)
5. Stitz, V. Biochem. Ztschr. Ztschr. Physiol. Chem. Berl. Ztschr. 32, 18, 7, 1, 19 (1911).
6. Zintl and Lumsden, Z. Chem. Chem. 216, 114, (1933).
7. Zintl, Thomsen, und Wolfbrandt, Chem. 38, 187 (1935).

REACTIONS BETWEEN SOLIDS

Nancy Downs December 19, 1944

Introduction.

Reactions between solids have been employed for many years in industry but the study of such reactions is of comparatively recent origin. Since the beginning of these studies, over five hundred scientists have investigated solid reactions, approximately thirty-five of whom have been English or American (1)(2). Most of the work has been done on the interaction of metals with each other or the interaction of metallic oxides with other oxides or salts such as halides, sulfates, and silicates. Some studies of double decomposition reactions have been made.

History.

First work was done by Spring (1)(2)(3), and Sir Roberts-Austin about 1895 (2). Later Masing studied the effect of pressure on metal filings in bringing about a reaction. Cobb began the research of non-metallic compounds about 1910 (2). He suggested that a "quasivaporous" theory could be used to explain solid reactions (2). Taradoire claimed that for two solids to react, one had to have a vapor pressure. Also it was believed that the reaction didn't take place in the solid state but in a fused state or a gaseous state (4). Our modern conception of solid reactions has been built largely by the work of Tammann, Jander, Jost, Huttig, Hedvall, Hume and Calvin, Fischbeck, Seith, and Tubandt, in Europe (3)(2) and Ward and Wood in the United States.

Mechanism of Solid Reactions.

A. Four Stages in a solid reaction (5)(6).

1. A reaction takes place at the point of contact. It results in an increase of catalytic action.
2. The second step is the formation of a thin reacting layer or reaction skin. With the formation of this skin, there is a decrease in catalytic action, an increase in ability to absorb dyes and an increase in solubility in weak reagents (7)(8)(5)(9)(11).
3. The third step is the change of reaction layer and the formation of defective crystals.
4. The last step is the transformation of the defective crystals into pure crystals.

The four stages take place at two different rates. At first the reaction goes very rapidly, then it slows tends to slow down (10). The explanation of the rapid reaction rests on the fact that in the preparation of the mixtures by grinding or because of impurities present in the crystal, some crystals are deformed. The molecules, atoms, or ions which are moved out of place can change positions more easily at a lower temperature than perfect crystals will and the reaction occurs rapidly until the deformations are removed by the reaction or by recrystallization. Then the reaction slows down. The rates of the reactions depend upon the rate of diffusion and the rate of crystallographic changes (1)(2)(3)(11)(12).

B. Diffusion in solids (1)(3)(13).

1. Diffusion may occur in solids in one of three ways (13).
   a. Particles may pass along internal surfaces.
   b. Particles may pass in interstitially within the normal lattice.
   c. They may pass as a result of the vacant places within the lattice and movement of adjacent particles into the vacant positions (12)(6).
2. Tammann's equation (14)(15).

   Derived from Fick's law which may be stated mathematically:

$$dn = -QK \frac{dy}{dx}$$

   By substitutions and integration the following expression is obtained.

$$n = b \log t + c$$

   where n = quantity of substance which diffuses in terric t
   b = fraction of "diffusion threads" broken during given time.
   t = time
   c = constant

   If the percentage decomposition is plated against log t., a straight line is obtained. This seems to indicate a direct relationship between percentage decomposition and the rate of diffusion. Applications to actual data seem to prove the validity.
3. Jander's equation (14).

   This equation relates the thickness of the layer to the percentage decomposition.

$$\left(1 - \sqrt[3]{\frac{100-x}{100}}\right)^2 = \frac{2DCot}{r^2}$$

   x = the percentage decomposition.
   2DCot = the square of the thickness of the reaction layer.

   If the $\left(100 - \sqrt[3]{\frac{100-x}{100}}\right)^2$ is plotted against t a straight line is obtained.
4. Hume, Calvin, Topley equation.

   This equation is based on their belief that a crystallographic change takes place in a solid (14)(16). The rate at which the crystallographic change takes place is dependent on (a) the rate of nucleation, (b) rate of propagation of interfaces between the solids. In turn, the rate of solid reactions depends on rate of crystallographic changes in addition to diffusion.

   The equation relates the fraction decomposed to the time. (14)

$$= (Kt)^3 - 3(Kt)^2 + 3Kt$$

   These equations were applied to experiments by Wood and his coworkers and were found to agree quite well with experimental results.

C. Temperature affects the rate of reaction since it affects both the rate of diffusion and the rate of crystallization.

<u>Classification of solid reactions</u> (1)

A. Two elements

$M' + M''$

B. Two binary compounds with a common component.
$M'X' + M''X'$ or $M'X' + M'X''$
An example is the reaction of CaO with SiO_2.

C. Two binary compounds without a common component.
$M'X' + M''X''$

The first two types have been investigated to the greatest degree and the latter type perhaps has been neglected because no accurate quantitative methods were known.

Double decomposition reactions in the solid state.

Early work was done by Plato and Ruff (19) and Berketoff (17). More recently Tammann (15), Hedrall (3), Mathieu, Mathieu, and Paic(19), have done research on such equations.

Roland Ward and coworkers (14)(18) studied reactions between alumina and barium sulfate, and between ferric oxide and barium carbonate. From the results they obtained and from information they obtained by comparing their results to the Jander, Tammann, and Hume-Calvin-Topley equations, they set forth the idea that perhaps it is possible for the rate of crystallographic transition to be the deciding factor in the rate of certain chemical reactions.

L. J. Wood and his coworkers (17)(20)(21)(22)(23)(24) did a series of experiments on the reactions of solid alkali halides both above and below the fusion point, using an x-ray spectrograph to record the results. The results may be summarized as follows:

A. At temperatures above the fusion point (17)(20)(21).
1. In fifty seven out of the sixty reactions, the reactions went in such a way that the average cube edge of the stable pair was less than that of the reciprocal pair.
2. In fifty-seven of the sixty reactions, the sum of the heats of formation of the stable pair is greater than the sum of the heats of formation of the reciprocal pair.
3. The cation of the larger atomic weight unites with the anion of the larger atomic weight and the cation of the smaller atomic weight unites with the anion of the smaller atomic weight.
4. With the exception of the lithium salts, one member of the stable pair has the highest melting point of any of the four compounds formed.
5. In fifty-seven of the sixty reactions the reaction goes to completion as evidenced by
   a. Absence of x-ray patterns for two of the compounds involved.
   b. The cube edge of a resulting solid solutions is the same as the theoretical cube edge.

B. At temperatures below the fusion point (22)(23)
1. In the twelve reaction mixtures containing lithium salts and fluorides, the stable pair always had as a member, lithium fluoride. The stable pair in six cases contained the highest melting compound and in six cases the reciprocal pair contained the highest melting point.
2. If no fluorides are present in the lithium salts, the highest melting compound was found in every case in the reciprocal pair.

3. In the reactions involving no lithium salts, but fluorides, the highest melting component was contained in the stable pair.
4. For fifty-four of the sixty reactions, there was a complete or partial conversion of the reciprocal pair to the stable pair.
5. Little reaction occurs if the temperature is more than 200° below the fusion point and the reaction proceeds quite rapidly if the temperature is within 100° of the fusion point.

BIBLIOGRAPHY

1. Jose, Wilhelm, "Diffusion and Chemische Reaktion in Festen-Stoffen", Leipzig (1937).
2. van Klooster, J. Chem. Ed., 17, 361-3 (1940)
3. Hedvall, J. A., "Reaktions fahigkeit fester Stoffe", Barth, Leipzig, (1938).
4. Taradoire, F., Bull. soc. chim., 6, 866-72 (1939).
5. Jander, W. and Weitendorf, K. F., Z. Elektrochem., 41, 435-44 (1935).
6. Jander, W. and Bunde, K., Z. anorg. allgem. chem., 231, 345-64 (1937).
7. Jander, W. and Schule, W., Z. anorg, allgem. chem., 214, 55-64 (1933)
8. Jander, W., Z. Ver deut, Ing. 80, 506-10 (1936)
9. Jander, W., Z. anorg. allgem. chem. 174, 11-23 (1928)
10. Ward R., Trans. Ill. Acad. Sci., 25, 167-9 (1933)
11. Huttig, G. F., Chem. Ztg. 61, 408-409 (1937)
12. Hedvall, J. A., Proc. Symposium on Chemistry of Cements, 42-57 Stockholm (1938).
13. Garner, W. E., Science Progress , 33, 209-229 (1938)
14. Ward, R., and Booth, H. S., J. Phys. Chem. 36, 961-84 (1932)
15. Tammann, Z. Angew. Chem. 39, 869-75 (1926)
16. Hume, J. and Colvin, J., Phil. Mag. 7 8, 589-96 (1929)
17. Wood, L. J. and Thomas, E. B., J. Am. Chem. Soc. 56, 92 (1934)
18. Ward, and Struthers, J. D., J. Am. Chem. Soc. 59, 1849 (1937)
19. Mmme. Mathieu, Mathieu, and Paci, Comp. rend. 192, 416 8 (1931)
20. Wood, L. J., and Thomas, E. B., J. Am. Chem. Soc. 57, 822 (1935)
21. Wood, L. J., and Thomas, E. B., J. Am. Chem. Soc. 58, 1341 (1936)
22. Wood, L. J., and Link, H. L., J. Am. Chem. Soc. 60, 2320 (1938)
23. Wood, L. J., and Link, H. L., J. Am. Chem. Soc. 62, 766 (1940)
24. Wood, L. J., and Vogt, J. W., J. Am. Chem. Soc. 66, 1259 (1944)

6. In the reactions involving no liquid water, but
[illegible], the slowest moving component was initiated
in the weakly polar.

4. For diffusion of the alkyl reactions, there was a
complete or partial interchange of the [illegible] polar
to the [illegible] polar.

5. Little reactivity occurs if the temperature is only than
200° below the fusion point and the reactivity [illegible]
quite regardless of the temperature is within 100° of the
fusion point.

BIBLIOGRAPHY

1. Jones, William, "Electrolyte and Covalente Reaction in Protonic Solvent", Lehigh [illegible].
2. von Klemperer, W. Chem. Ed., 37, 281-3 (1960)
3. Edwards, J. O., "Inorganic Physical Chemistry Series", Butterworths, London. (1962).
4. Jander, J., Z. anorg. allg. Chem., 6, 266-72 (1959).
5. Jander, W. and Wistrocil, E. Z., Z. Elektrochem., 61, 108-14 (1957).
6. Jander, W. and Bauer, E., Z. anorg. allgem. Chem., 301, 240-64 (1959).
7. Jander, W. and Brunig, G., Z. anorg. allgem. Chem., 314, 58-64 (1962).
8. Jander, W., Z. Ver. dtsch. Ing., 50, 664-7 (1956)
9. Jander, W., Z. anorg. allgem. Chem., 279, 11-22 (1955)
10. Bard A. J., Chem. Rev., 66, 757-9 (1966)
11. Butler, J. N., Chem. Rev., 68, 375-90 (1968)
12. Murray, J. G., Proc. Symposium on Electrolyte of Somerset, 15-27 Brookhaven (1959).
13. Barnes, W. S., Science Frontiers, 16, 214-21 (1966)
14. Mark, H., and Rudko, H., J. Chem. Educ., 35, 382-84 (1958)
15. Cassman, T., Anal. Chem., 41, 288-91 (1969)
16. Kern, D. and Calvin, M., J. Chem. Phys., 9, 486-94 (1941)
17. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
18. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
19. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
20. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
21. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
22. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
23. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
24. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
25. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
26. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
27. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
28. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
29. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
30. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
31. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
32. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
33. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)
34. Wood, L. J., and Gillam, R. E., J. Am. Chem. Soc., 78, 1836 (1956)

INORGANIC CATALYSIS; INDUCED REACTION, PRECIPITATION, AND SOLUTION

F. W. Cagle, Jr. January 2, 1945

While the action of a catalyst either accelerates or diminishes the rate at which a reaction proceeds, it must be firmly understood that the presence of this catalyst in no fashion effects the extent to which the reaction will take place. The equilibrium conditions are uniquely determined for every reaction by the concentrations of the reactants and a choice of sufficient physical conditions. The calculation of this position of equilibrium is in the province of thermodynamics and if proper thermodynamic data are given, it can be calculated for any reaction for which the reactants and final products are known. This may be done without consideration of the intermediate products of the reaction.

In the field of rates of reaction, in which the art of catalysis finds its place, one discovers no "broad highway" which leads to success. In fact, one cannot set down a single general law or principle of catalysis. It is for this reason that the writer refers to catalysis (and related phenomena) as an art rather than a science. Knowing these things, we shall discuss catalysis only so far as the science is known and not attempt to draw general conclusions nor expect to see general principles resulting from this discussion.

The writer further desires to introduce with catalysis the induced reaction in which the "catalyst" suffers change in the reaction, for it seems that the exclusion of this kindred phenomenon would be not only highly arbitrary but objectionable as well. For the same reason, the phenomenon of induced precipitation and solution will be discussed.

It is of course evident that if a reaction could be found which is catalyzed by a certain element or radical in a mixture but not catalyzed by other substances, one could detect very small amounts of the catalyst by observing its effect upon the reaction.

1. Catalysis Due to Complex Formation

   a. The reduction of Ce^{+4} salts by dilute HCl proceeds very slowly at room temperature. This may be much accelerated by the formation of $HgAgCl_2$ (1,2).

   b. Chlorates in a neutral or mildly acid solution are only very weak oxidizing agents. The addition of a trace of OsO_4 suffices to make them behave as powerful oxidizing agents. It can be shown that the solubility of $KClO_3$ is markedly greater in neutral OsO_4 solutions than in water. Further the oxidation potential of such a solution is much greater than that of a solution of $KClO_3$ alone. This has been interpreted as indicative of the formation of a complex $KClO_3$-OsO_4 (3, 4, 5).

2. Catalysis Due to Principal Valence Compounds Compounds

a. $H_2O_2 + Na_2S_2O_3 + 2HC_2H_3O_2 = Na_2S_4O_6 + 2NaC_2H_3O_2 + 2H_2O$
but with a trace of $MoO_4^{=}$ (6)

$4H_2O_2 + Na_2S_2O_3 = 3H_2O + Na_2SO_4 + H_2SO_4$

The same effect may be achieved with tungstates, vanadates, and zirconium, thorium, and titanium salts (7).

b. $2H_3AsO_4 + 10H^+ + 4I^- = 2As^{+3} + 2I_2 + 8H_2O$

$2As^{+3} + 3H_2S = \underline{As_2S_3} + 6H^+$

$2I_2 + 2H_2S = 4I^- + 2S + 4H^+$

These reactions of catalytic nature are used in qualitative analysis in order to avoid the slow precipitation of As_2S_5 (8).

c. $2NaN_3 + I_2 = 2NaI + 3N_2$

This reaction is quite slow but very greatly accelerated by $S^{=}$ in many forms (9, 10).

d. The salts of Cu^{++} enjoy the distinction of acting as catalysts in both oxidation and reduction reactions. This is due no doubt to the formation of relatively unstable Cu^{+++} salts in the first case and Cu^{+} salts in the second case.

An example of the use of copper salts as oxidizing catalysts is found in the oxidation of manganous ion to permanganate by hypobromite. Unless a trace of a copper salt is present, manganous dioxide (not permanganate) results (11).

The reaction between the ferric ion and thiosulphate ion ($2Fe^{+++} + 2S_2O_3^{=} = 2Fe^{++} + S_4O_6^{=}$) is very greatly accelerated by a very slight trace of a cupric salt. This reaction illustrates the role of Cu^{+} as a catalyst in reduction reactions (12).

3. Induced Reactions

If a reaction velocity is augmented by the occurrence of another (apparently unrelated) reaction which occurs at the same time as or just before the first reaction, that first reaction is said to be an induced reaction (13).

a. The classical example of an induced reaction is the oxidation of sodium arsenite solution by the oxygen of the air (this reaction proceeds by itself too slowly to be measured) in the presence of a sulphite which is itself being oxidized to a sulphate.

According to the classical nomenclature of Kessler, we may consider this induced reaction in two steps:
$2SO_3^{=} + O_2 = 2SO_4^{=}$ (inducing reaction)
$2AsO_3^{\equiv} + O_2 = 2AsO_4^{\equiv}$ (induced reaction)

Such coupled reactions have a common component (O_2 in this case) called the actor. The material in the inducing reaction which reacts with the actor is called the inductor ($SO_3^{=}$), and the substance which thereby undergoes chemical changes in the induced reaction is called the acceptor (AsO_3). If we define a term called induction factor which is the ratio of oxidized equivalents of the acceptor to oxidized equivalents of the inductor, we may observe that the greater this value becomes the more nearly catalytic the reaction appears to be. Thus, the fields of induced reaction and catalytic reaction tend to merge.

An example of an induced reaction with a high induction factor is the oxidation of oxalic acid by mercuric chloride (in a solution of proper concentration this does not occur at a measurable rate) induced by the oxidation of some of the oxalic acid by permanganate. In the presence of a trace of permanganate a copious precipitate of mercurous chloride is soon formed (14).

4. Induced Precipitation and Solution.

A substance which would not normally precipitate under a given set of experimental conditions will sometimes co-precipitate with another substance. The phenomenon is called induced precipitation. Conversely it is occasionally possible to effect the solution of a substance not normally soluble in a given reagent by simply allowing the reagent to react with a mixture of that substance and another substance soluble in the reagent.

An example of induced precipitation is the crystallization of lead sulphate from solution in acetic acid and ammonium acetate by the formation of a trace of barium sulphate in the solution.

The phenomenon of induced solution is shown by the ability of a solution of dilute nitric and tartaric acids to dissolve completely and rapidly an alloy of tin and antimony. Tin alone gives metastannic acid.

References:

1. F. Feigl and Frankel, Ber., 65, 544 (1932).
2. F. Feigl, Spot Tests, 2nd Engl. Ed., Nordemann Publishing Co., New York, 1939, p. 20.
3. K. Hofmann, Ber. 45, 3329 (1912)
4. Hofmann, Ehrhart, and Schneider, Ber., 46, 1658 (1913).
5. F. Feigl, Op. Cit., p. 81.
6. E. Abel, Z. Electrochem., 19, 480 (1913).
7. F. Feigl, Z. angew. Chem., 44, 741 (1931).
8. J. Reedy, Theoretical Quantative Analysis, McGraw-Hill Book Co., New York, 1938, p. 212.
9. F. Raschig, Ber., 48, 2088 (1915).
10. F. Feigl, Op. Cit. p. 195 ff.
11. K. Filimanowitsch, Chem. Abstr., 25, 5640 (1931).
12. Hahn and Leimback, Ber., 55, 3070 (1922)
13. A. Skrabal, Die Indutzierten Reaktionen, ihre Geschichte und Theorie, Stuttgart, 1908.
14. F. Feigl, Op, Cit., p. 138.
15. F. Feigl, Z. angew.Chem., 43, 550 (1930)
16. A.Czerwek, Z. anal. Chem., 45, 505 (1906).
See also the very excellent discussion of this subject by F. Feigl. Specific and Special Reactions, Elseview Publishing Co., New York, 1940, p. 65 ff.

THE BORON HYDRIDES

Margaret Kramer January 9, 1945

I. Introduction:

About 1810, Davy noticed that the mass obtained in the preparation of boron by reduction of B_2O_5 with potassium when treated with water or dilute HCl produced a gas which was mainly hydrogen, but which has a disagreeable odor and which burned with a blue flame tinged with green. Wohler, H. St.C. Deville (1858), and Moissan (1893), among others, tried to prepare boron hydride by action of dilute HCl on aluminum boride or by direct union, or by other means, but without success(10).

Jones (1879) obtained a mixture of the hydrides by treating magnesium boride with acids. In 1901 Ramsey and Hatfield demonstrated the gas was a mixture of several hydrides condensed by liquid air (13).

From about 1912 until 1931 most of the work on the born hydrides was done by Stock and coworkers (19). Since 1931 other investigators have entered the field, and their further work has resulted in improved methods of preparation for the hydrides as well as an elucidation of their structures.

Since boron is a trivalent element, its simplest hydride should be BH_3. Such a compound has not been isolated, however, the simplest boron hydride capable of independent existence being B_2H_6. In certain chemical reactions B_2H_6 gives evidence of being composed of BH_3 units. Burg and Schlesinger (5) have noted that linkages between boron atoms seldom occur in compounds of boron with elements other than hydrogen. The tendency for such linking is so strong that BH_3 does not exist.

According to older theories of valency, boron should form hydrides of the general formula B_nH_{n+2}(16). The boron hydrides now known are B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$. Such a general formula does not apply.

The advent of the electron theory of valency did not at first improve matters. If one assumes B_2H_6 to have an ethane-like structure, 14 valence electrons are required, while B_2H_6 can muster only 12.

The result of this abnormality has been increased research on the boron hydrides, their chemistry and their structures.

II. Preparation:

The first hydride prepared by Stock, using a special technique involving high vacuum and low temperature distillation, was B_4H_{10}. The yield was rather small, and other heavier hydrides of boron were in the reaction product as well (19).

$$6Mg + B_2O_3 \longrightarrow Mg_3B_2 + 3MgO$$

$$Mg_3B_2 \xrightarrow{10\%\ HCl} B_4H_{10} + \text{traces of } B_5H_9,\ B_6H_{10},\ B_{10}H_{14} \quad (26)$$

THE BORON HYDRIDES

Margaret Kinney January 5, 1943

I. Introduction:

About 1825, Dary obtained what its was solution in the preparation of borax by reduction of B_2O_3 with potassium when treated with water or alcohol. Dri produced a gas which was mainly hydrogen, but which was a disagreeable odor and which burned with a blue flame tinged with green. Stock, H. Ff.G. Davlin (1909), and Moissan (1909), among others, tried to prepare boron hydride by reduction of chloride but no alumina hydride or by direct action, or by silent sparks, but without success(10).

Jones (1937) obtained a mixture of the hydrides by treating magnesium boride with acids. In 1938 Hurd and Bartlett obtained the gas was a mixture of mainly hydrides condensed by liquid air (12).

From about 1912 until 1933 most of the work on the boron hydrides was done by Stock and coworkers (11). Stock and other investigators found the first, and their chemist were the pioneers in improved methods of preparation for the hydrides as well as in elucidation of their structures.

Diborane is a colorless gas, its molecular formula should be B_2H_6. Stock's proposed has not been included, however, the molecular formula, regardless of isomerism is satisfactory being B_2H_6, in results obtained (Stock, Ulicher B_2H_6 gives evidence of being composed of BH_3 units. Hurd and Coolidge (2) have noted that diborane between where other hydrides occur in sequence of boron with elements of the hydrogen. The tendency for each hydrogen is to attach itself to a boron atom.

According to other theories of valence, boron should form hydrides of the general formula B_nH_{n+4}(12). The boron hydrides are colorless, odorless, highly toxic, B_2H_6, and B_4H_{10}. Stock's general formula does not apply.

The action of the electron theory of valency did not at first throw light on the structure. If the electron B_2H_6 is more or otherwise circumstances, in which electrons are required, while B_4H_{10} can satisfy only 12.

The result of this discrepancy has been increased research on the boron hydrides, their chemistry and their structures.

II. Preparation:

The first hydride prepared by Stock, using a special technique involving high vacuum and low temperature distillation, was B_2H_6. The yield was rather small, and other methods of preparation of boron were the reaction (which) as well (12).

$$BCl_3 + 3H_2 \longrightarrow B_2H_6 + 6HCl$$

$$B_2O_3 + 3H_2 \longrightarrow B_2H_6 + 3H_2O$$

$$B_2O_3 + 6HCl \longrightarrow 2BCl_3 + 3H_2O, \quad 2BCl_3 + 3H_2 \longrightarrow B_2H_6 + 6HCl \quad (10)$$

Wiberg and Schuster found that 8N H_3PO_4 increased the yield from about 4% to 11% (28). Upon heating at 100°, the hydride forms B_2H_6 and small amounts of B_5H_9 and $B_{10}H_{14}$ (7).

A second method for the preparation is:

$$B_5H_{11} \xrightarrow[1.5\ atm.]{100°} \underset{85\%}{B_4H_{10}} + B_2H_6 \quad (4)$$

B. B_2H_6 is most simply prepared by action of hydrogen on boron trichloride under suitable conditions (3).

Pure hydrogen is bubbled through liquid BCl_3 at -40°C. and the resulting mixture is passed through a 12-15 kilovolt discharge formed between water cooled copper electrodes. The pressure is maintained between 5 and 10 mm. The products are much unchanged boron trichloride and hydrogen, together with B_2H_5Cl and a small amount of B_2H_6. The mixture is condensed from excess hydrogen and fractionated to remove HCl. At a pressure of 2 mm. at 0°C, B_2H_5Cl decomposes:

$$6B_2H_5Cl \rightleftharpoons 5B_2H_6 + 2BCl_3$$

The diborane is removed as fast as it is formed. Fractions rich in hydrides are further fractionated and the resulting B_2H_6 is finally purified by vacuum distillation at -150°C.

The method may be improved by using BBr_3 instead of BCl_3, the resulting HBr being more easily removed. BBr_3 is less volatile than BCl_3 (122). Yields as high as 80% of the halide reacting have been reported.

C. Other boranes are prepared by heating B_2H_6 under suitable conditions..

$$B_2H_6 \xrightarrow{115°} H_2 + B_4H_{10} + \underset{\text{(Main product)}}{B_5H_{11}} \quad (4)$$

$$B_2H_6 \xrightarrow[180°]{\text{high vac.}} B_5H_{11} + B_4H_{10} \quad (23)$$

$$B_2H_6 \xrightarrow[\substack{250°-300° \\ \text{Hg vapor}}]{120\ mm.} B_5H_{11} + \underset{\text{(Main product)}}{B_5H_9} \quad (23)$$

$$B_2H_6 \xrightarrow[\substack{160°,\ \text{slightly above atmos.} \\ \text{pressure.}}]{\text{sealed tube}} B_4H_{10} \quad (19)$$

$$B_4H_{10} \xrightarrow[\text{vacuum}]{90-95°} B_{10}H_{14} \quad (19)$$

B_6H_{10} was prepared by Stock and Massenez (24) in small quantities from the crude gas appearing upon decomposition of magnesium boride with acid,

I. Properties (see table 1):

A. Thermal stabilities

1. B_5H_{11} least stable.

$$B_5H_{11} \longrightarrow B_2H_6 + B_4H_{10} + H_2 + B_5H_9 + B_{10}H_{14} \quad (4)$$

2. B_2H_6, stable, decomposes at 100° or above.

$$B_2H_6 \longrightarrow B_4H_{10} + B_5H_{11} + B_5H_9 + B_{10}H_{14} \quad (2)$$

3. $B_6H_{10} \xrightarrow[\text{temp.}]{\text{ord.}} B_2H_6 + H_2 + B_{28}H_{56}$ (20)

4. B_5H_9, stable up to 150°. (16)
5. $B_{10}H_{14}$, stable up to 170°. (16)

B. Chemical reactions (16, 19).

1. Oxygen

B_5H_{11} and B_5H_9 burn spontaneously at ordinary temperatures. $B_{10}H_{14}$ explodes at 100°. B_6H_{10} is only slowly affected by air. B_2H_6 and B_4H_{10} react above room temperatures. The products of the reactions are of indefinite composition.

2. Water

The boron hydrides are hydrolyzed by water to produce boric acid and hydrogen.

The mechanisms of the reactions have not been established. Wiberg suggests no less than 10 steps in the reaction of diborance with water. Of the 9 compounds formed, 5 are unknown, and 3 are hypothetical (16, 29).

3. Halogens (19)

Diborane, stable pentaborane, and decaborane react with the halogens to produce substituted boranes.

4. Hydrogen halides (19)

Diborane and tetraborane react with hydrogen halides to produce substituted boranes. The reactions proceed in the presence of aluminum chloride.

Stable pentaborane and decaborane do not react.

5. Ammonia (16, 19).

Under carefully controlled conditions, diborane reacts to produce a diammonia derivative:

$$B_2H_6 + 2NH_3 \xrightarrow{-120°C} B_2H_6.2NH_3$$

For this compound the structures $(NH_4)_2(H_2B::BH_2)$ and

$$NH_4 \quad H_2B:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{N}}:BH_3$$

Upon heating, the two products produce $B_3N_3H_6$, with a ring structure.

6. Metals (16)

Sodium, potassium, and calcium react with diborane to give compounds of the type $M_2B_2H_6$, where M is a monovalent metal. B_4H_{10} reacts with sodium. B_2H_5I reacts also with sodium.

$$B_2H_5I + 2Na \longrightarrow B_4H_{10} + 2NaI \quad (125)$$

2. Ta_2Br_6, stable, decomposes at 100° or above.

Ta_2Br_6 reacts: $Ta_2Br_6 + Ta_2Br_6 \rightarrow Ta_4Br_{12}$ (1)

3. $Ta_2Cl_6 \xrightarrow[\text{heat}]{\text{Ta}} Ta_3Cl_8 + Ta + TaCl_4$ (20)

4. Ta_3Br_8 stable up to 200°. [19]

5. Ta_2Br_5 stable up to 170°. [19]

C. Chemical properties (18, 19).

1. Oxygen

Ta_4Cl_{12} and Ta_4Br_{12} burn spontaneously at ordinary temperatures. Ta_3Br_8 ignites at 300°. Ta_2Br_5 is only slowly attacked by air. Ta_2Cl_6 and Ta_2Br_6 react above 200 temperatures. The products of the reactions are of indefinite composition.

2. Water

The lower chlorides are hydrolyzed by water to produce boric acid and hydrogen.

The behaviour of the tantalum bromides has been partially. Without accurate data that has to about 10 atom% the reaction of chlorides with water, of the 3 compounds formed, 2 are solvent, and 3 are insoluble [19, 20].

3. Halogens (20)

Chlorine, stable pentachloride, and decomposes more with the halogens to produce substituted bromides.

4. Hydrogen halides [21]

Bromides and iodides react with hydrogen halides to produce substituted chlorides. The reactions proceed in the presence of aluminum chloride.

Stable pentachloride and hydrogen do not react.

D. Amines (22, 23).

Water carrying terminal amidities, diborane reacts to produce a diamino derivative:

$Ta_4Br_{12} + 2NH_3 \rightarrow Ta_4Br_{10}(NH_2)_2$

For this reaction the structure $[Ta_4Br_{10}(NH_2)_2]$ has

$$Ta_4 \quad Br_{10}(NH_2)_2$$

$$\|$$

open chain, like the product $[Ta_2Br_4]$, with a ring structure.

E. Metals [24]

Sodium, potassium, and rubidium react with diborane to give compounds of the type Ta_2Br_5, where X is a monovalent metal. Ta_2Br_5 reacts with sodium, Ta_2Br_5 reacts also with sodium.

$$Ta_2Br_5 + Na \longrightarrow Ta_2Br_4 + NaBr \quad (24)$$

7. Metallo boronhydrides (6, 15, 17)

These are prepared by action of B_2H_6 on alkyl compounds of lithium, beryllium, and aluminum.

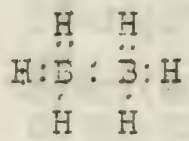
$$2C_2H_5Li + 2B_2H_6 \longrightarrow LiBH_4 + (C_2H_5)_2B_2H_4$$

8. Coordination compounds (8, 16)

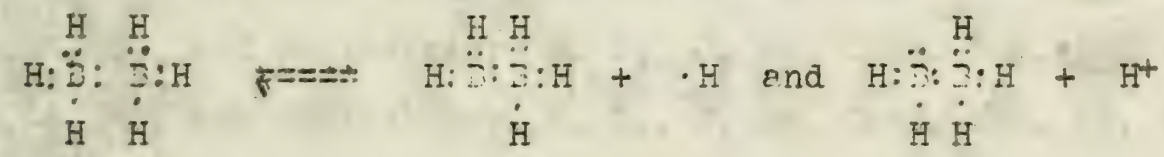
At relatively low temperatures B_2H_6 reacts to produce coordination compounds of borine (BH_3). The following compounds react to form the coordination compounds: $(CH_3)_3N$, CH_3NH_2, $(CH_3)_2NH$, CO, $(CH_3)_2O$, PH_3, CH_3CN, and C_6H_5N.

IV. Structure

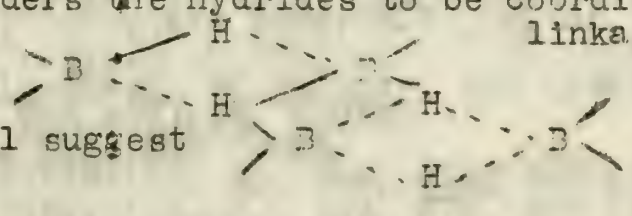
A. Sidgwick has proposed single electron bonds in the structure of B_2H_6 (18).



B. Pauling considers such a structure possible under the following conditions: "a stable electron bond can be formed only when there are two conceivable electronic states of the system, with essentially the same energy states differing in that for one there is an unpaired electron attached to one atom and for the other the same unpaired electron is attached to the second atom" (14). Resonance produces a stable molecule.



C. Bauer (2), using electron diffraction methods concludes that diborane has an ethane-like structure, tetraborane a butane-like structure, unstable pentaborane either a pentane- or iso-pentane-like structure. Stable pentaborane was assigned a methylene cyclobutane structure. Hexaborane is said to have a dimethyl-clyclobutane-like structure. Decaborane is said to have a double 4-membered ring with BH_3 groups at the two ends:

D. Nekrasov (11, 12) considers the hydrides to be coordination compounds held together by  linkages.

Longuet-Higgins and Bell suggest linkages (9).

Wagner discounts the ethane structure for diborane, suggesting instead an ethylene-like structure (27).

$H_2BH_2BH_2$.

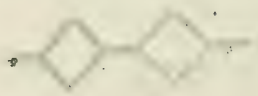


TABLE 1 (16)

PHYSICAL CONSTANTS OF THE BORANES

Name	Molecular Formula	Density	Melting Point	Boiling Point	Vapor Tension
			°C	°C	Mm
Diborane	B_2H_6	0.577(-183°C) 0.477(-112°C)	-165.5	-92.5	225(-119.9°C)
Tetraborane	B_4H_{10}	0.56 (-35°C)	-120	18	388 (0°C)
Stable Pentaborane	B_5H_9	0.61 (0°C)	46.6	48	66 (0°C)
Unstable Pentaborane	B_5H_{11}		-123	63	53 (0°C)
Hexaborane	B_6H_{10}	0.69 (0°C)	- 65		7.2 (0°C)
Decaborane	$B_{10}H_{14}$	0.92 (99 °C) 0.78 (100°C)	99.7	213	19 (100°C)

BIBLIOGRAPHY

1. Bauer, S. H., J. Am. Chem. Soc., 60, 805 (1940).
2. Bauer, S. H., Chem. Rev. 31, 43 (1942).
3. Burg, A. B., and Schlesinger, H. I., J. Am. Chem. Soc. 53, 4321 (1931).
4. Burg, A. B., and Schlesinger, H. I., J. Am. Chem. Soc. 55, 4009 (1933).
5. Burg, A. B., and Schlesinger, H. I., J. Am. Chem. Soc. 55, 4020 (1933).
6. Burg, A. B., and Schlesinger, H. I., J. Am. Chem. Soc. 62, 3425 (1940).
7. Emeleus, H.J., Annual Reports on the Progress of Chemistry, 139 (1940
8. Gamble, E. L., and Gilmont, P. L., J. Am. Chem. Soc. 62, 717 (1940)
9. Longuet-Higgins, H.C., and Bell, R.P., J. Chem. Soc. 250 (1943).
10. Mellor, J.W., Comprehensive Treatise on Inorganic and Theoretical Chemistry, V.5, 33 (1922-1937)
11. Nekrasov, B.V., J. Gen. Chem. (USSR) 10, 1021 (1940).
12. Nekrasov, B.V., J. Gen. Chem. (USSR) 10, 1156 (1940).
13. Partington, J.R., A Textbook of Inorganic Chemistry, 7720 (1933).
14. Pauling, L., J. Am. Chem. Soc. 53, 3225 (1931).
15. Schlesinger, H.I., and Brown, H.C., J. Am. Chem. Soc. 62, 3429 (1940)
16. Schlesinger, H.I., and Burg, A.B., Chem. Rev. 31, 1 (1942).
17. Schlesinger, H.I., Sanderson, R.T., and Burg, A.B., J. Am. Chem. Soc. 62, 3421 (1940).
18. Sidgwick, N.V., The Electronic Theory of Valency, 103 (1927).
19. Stock, A., Hydrides of Boron and Silicon, (1933)
20. Stock, A., and Kuss, E., Ber. 56B, 789 (1923)
21. Stock, A., Martini, H., and Sutterlin, W., Ber. 67B, 396 (1934).
22. Stock, A., Martini, H., and Sutterlin, W., Ber. 67B, 407 (1934).
23. Stock, A., and Mathing, W., Ber. 69B, 1456 (1936)
24. Stock, A., and Massenez, C., Ber. 45, 3529 (1912)
25. Stock, A., and Pohland, E., Ber. 59B, 2215 (1926).
26. Stock, A., Wiberg, E., and Martini, H., Z. Anorg. Allgem. Chem. 188, 32 (1930).
27. Wagner, J., Z. Physik. Chem. B53, 85 (1943).
28. Wiberg, E. and Schuster, K., Ber. 67B, 1805 (1934).
29. Wiberg, E., Ber. 69B, 2816 (1936)

A SURVEY OF INORGANIC NITRIDES; PROPERTIES, PREPARATION, AND REACTIONS

Lawrence J. Edwards January 16, 1945

I. General Consideration.

The affinity of nitrogen for other elements is not manifested at ordinary temperatures, but on heating combination often occurs. Combination of a metal and nitrogen is usually exothermic, whereas the formation of a non-metallic nitride is the result of an endothermic reaction (23). The formulas of the nitrides, in the cases where they have been definitely established, are usually those which are to be expected from the ordinary valency of the second element and the tri-valency of nitrogen. Consequently, nitrides can be regarded as salts derived from the anhydro-acid ammonia.

II. Various Methods of Preparation and General Properties.

1. Direct Combination.

Generally, direct combination takes place at moderate or high temperatures with the element or amalgams of the element. Thus, Li, Mg, Ca, Sr, Be, B, Al, Si, Ti, Zn, V, Nb, Cb, Ta, Cr, U, Mn, and some of the rare earths have been prepared by this method. Lithium is rather unique in that it gives the nitride at a red heat (21)(10) and even in the cold (3). Amalgams of the alkaline earths are heated in atmosphere of nitrogen (17). Metallic Lanthanum absorbs nitrogen but sometimes in no definite proportions (20). The nitride of these reactive metals are dark powders easily hydrolyzed by cold water (9)(18). Ti, Ta, Zr, Hf and Cb nitrides conduct an electric current without decomposition and because of their high melting points, they are suitable for arc lamp electrodes or for cathode tubes or discharge tubes (1).

2. The Action of Carbon and Nitrogen on Oxides.

AlN is formed when aluminum oxide, mixed with carbon, is heated to a high temperature in a current of nitrogen. However, this procedure sometimes gives in addition, cyanide and cyanamide (9).

3. The Action of Gaseous Ammonia on Metals or Their Oxides.

When ammonia is passed over cupric or cuprous oxide at 300°C, a nitride, having the composition Cu_3N can be separated (2). However, using zinc dust and ammonia, the product contains less nitrogen than is required by the formula Zn_3N_2 (20). Nitrides of Fe, Ni, and Co give variable compositions (2)(4)(7)(19).

4. The Decomposition of Amides and Imides by Heat.

Each of the intermediate compounds has been isolated, and the conditions of the successive changes determined in the case of arsenic (13).

$$2As(NH_2)_3 \xrightarrow{60°C} As_2(NH)_3 + 3NH_3$$
$$As_2(NH)_3 \xrightarrow{250°C} 2AsN + NH_3$$

A Survey of Inorganic Activity: Ferroelectric, Piezoelectric, and Magnetic

Lawrence J. Edwards January 14, 1964

I. General Considerations.

The activity of ultrasonic for other elements is not sufficient at ordinary temperatures, but on heating considerable occurs. Combination of a metal and nitrogen in equal atomic proportions, the formation of a non-metallic activity is the result of an endothermic reaction (12). The formation of the nitrides, in the cases where they have been particularly studied, are usually those which are in be extracted from the industry without of the metal always not the formation of nitrogen. Consequently, nitrides can be regarded as only derived from the anhydro-acid analogs.

II. Various Methods of Preparation and Physical Properties.

A. Direct Combination.

Generally, direct combination takes place at different or high temperatures with the elements or analogues of the element. Thus, Li, Na, Ca, Sr, Ba, B, Al, Si, Ti, Zr, Nb, Ga, Ge, Y, Th, and many of the rare earth metals have prepared by this method. Lithium is another metal that it forms the nitride at 1 and lower (23)(32) and even in the air (1). Analogous of the alkaline earths are formed in atmosphere of nitrogen (17). Thermite reactions activity nitrogen not sometimes is an metallic reactions (30).

The nitride of alkali metals and alkaline earths are dark-green solids hydrolized by cold water (3)(20). Ti, Ta, Zr, Nb and Cr nitride evolves an electric current without decomposition and because of their high melting points, they are suitable for arc lamp electrodes or for electrode tubes in electronic tubes (4).

B. The Nitrides of Carbon and Silicon in Gases.

Air is filled also nitrides which, mixed with carbon, is heated to a high temperature in a current of nitrogen. However, this preparation accompanies given in cobalt, graphite and spectrals (9).

C. The Action of Gaseous Ammonia on Metals or Their Oxides.

When ammonia is passed over metals in a tubes cells at 300°C, a nitride, having the composition Cu_3N or Fe appeared (2). However, nitrid also that and ammonia. In product contains less nitrogen than is obtained by the treating CaO, (30). Nitrides of Fe, Mn, and Zr give nitrid variable composition (4)(6)(7)(12).

D. The Decomposition of Nitrides and Nitrides by Heat.

Most of the interstitial compounds can be been identified and the conditions of the adsorptive changes determined in the case of arsenic (10).

Zn_3N_2 $Zn_3N_2 \rightarrow 3Zn + N_2$ (100)

Mn_4N $Mn_4N \rightarrow 4Mn + N_2$ (50)

5. Action of Aqueous Ammonia.

Aqueous ammonia at ordinary temperatures converts the oxides of silver and gold into the explosive nitrides, Ag_3N, Au_3N, and Au_3N_2.

6. Reactions in Liquid Nitrogen.

The nitrides of tin, lead and cadmium have been prepared by passing an electric arc between electrodes of the metals immersed in liquid nitrogen (5),(6).

7. Reactions in Liquid Ammonia.

Double decompositions which occur between halides and amides in liquid ammonia generally yield complex double amides, frequently with ammonia of crystallization (8).

$$BiBr_3 + 3KNH_2 \longrightarrow BiN + 3KBr + 2NH_3$$

8. The Action of Dry Ammonia on Anhydrous Chlorides.

This type of reaction is applicable more to the chlorides of the non-metals, and especially those of Groups five and six of the periodic table.

II. Miscellaneous.

1. Transition vs. Non-Transition Elements.

Hagg (11) found that binary compounds between metals and nitrogen had metallic properties when the metal is a transition element; non-metallic properties are shown when the metal is not a transition element. Klemm and Schuth (14) found similar results from magnetic susceptibilities. In the series of elements from Scandium to Nickel with increasing atomic numbers, the stability of the compounds formed between these elements and nitrogen decreases. In the transition elements, if the ratio of atomic radii (rm/rn) is greater than 1.7, the structure becomes more complex, the smaller the radius of the metal ion (12). Vanadium iron, copper, and tungsten do not absorb nitrogen up to 125°, molybdenum absorbs only a small amount. The absorption of nitrogen begins at 780° for Mg and Ca, at 800° for Al and Cr, at 850° for Mn and at 900° for Ti (28). Mg, Ca, and Al give nitrides with definite formulae, while Ti, Cr, and Mn seem to form solid solutions of nitrogen in the metal.

2. Rate of Reaction and Heats of Formation.

The determination of the rate of reaction, of the formation of a nitride by "direct combination" is based upon the color changes of the metal in contact with the gas (24). By plotting a curve of the known heats of formations of some of the nitrides against the corresponding atomic number, the heats of formation of some of the less easily determined nitrides can be obtained by interpolation (15).

3. Decomposition Pressure and Temperature.

Lorenz and Woolcock (18) measured the decomposition pressure of BN between 1695 and 2045°C. They found the reaction to be reversible and by plotting Log p vs. 1/T, they got a straight line. Similar investigations with

yranium and nitrogen indicated the formation of U_5N_4 and U_5N_2. An investigation conducted by Voznesenskii (25) showed that the more simple the composition of the nitride, and the smaller the atomic volume of its nitride, the higher is its decomposition temperature and consequently the more stable it is to the action of various reagents.

4. Phosphorus Chloronitrides.

When an equimolal mixture of phosphorus pentachloride and ammonium chloride are heated together in a closed tube at 150°, a curious series of compounds is formed, the general formula of which may be designated by $(PNCl_2)_n$, where n = 3, 4, 5, 6, 7 and higher (22)(27). All members of this series seem to be non-polar in character. Due to symmetries in $(PNCl_2)_5$ and $(PNCl_2)_7$, these two compounds have remarkably low melting points. This series of phosphorus chloronitrides reacts only slowly even with boiling water. The rate of hydrolysis can be increased by the addition of a little ether to the water. Upon hydrolysis, these compounds yield hydroxy derivatives $[PN(OH)_2]_n$.

References.

1. Agte and Moers, Z. anorg. allgem. Chem. 198, 288 (1931); C. A. 25, 4480 (1931).
2. Beilby and Henderson, J. Chem. Soc. 71, 1252 (1901).
3. Deslandres, Compt. rend. 114, 120 (1892).
4. Despretz, Ann. chim. Phys. 42, 122 (1829).
5. Fischer and Ilionici, Ber. 41, 3802, 4449 (1908).
6. Fischer and Schroter, ibid., 43, 1465 (1910).
7. Fowler, J. Chem. Soc. 79, 285 (1901).
8. Franklin, J. Am. Chem. Soc. 27, 220 (1905).
9. Friederich and Settig, Zeitsch anorg. Chem. 143, 293 (1925); C. A. 19, 1669 (1925).
10. Guntz, Compt. rend. 120, 77 (1895).
11. Hagg, Z. physik. Chem. B6, 221 (1930); C. A. 24, 1591 (1930).
12. Hagg, ibid., B12, 33 (1931); C. A. 25, 2615 (1931).
13. Hugot, Compt. rend. 139, 54 (1904).
14. Klemm and Schuth, Z. anorg. allgem. Chem. 201, 24 (1931); C. A. 26, 887 (1932).
15. Kroger and Kunz, ibid., 218, 379 (1934); C. A. 28, 7134 (1934).
16. Lorenz and Woolcock, ibid. 176, 289 (1928); C. A. 23, 1343 (1929)
17. Macquenne, Compt. rend. 114, 25 (1892).
18. Montemartini and Losana, Grom. chim. ind. applicata 6, 323 (1924); C. A. 18, 3329 (1924).
19. Mute and Kirschbraun, J. Am. Chem. Soc. 28, 1343 (1906).
20. Muthmann and Kraft, Ann. 325, 261 (1902).
21. Ouvrard, Compt. rend. 114, 120 (1892).
22. Stokes, Am. Chem. J. 19, 782 (1897)
23. Strutt, Proc. Roy. Soc. 85, 219 (1911); 87, 180 (1912).
24. Tammann, Z. anorg. allgem. Chem. 124, 25 (1922); C. A. 17, 14 (1923).
25. Voznesenskii, J. Russ. Phys. Chem. Soc. 61, 1323 (1929); C. A. 24, 4902 (1930).
26. White and Kirschbraun, J. Am. Chem. Soc. 28, 1343 (1906).
27. Yost and Russell, "Systematic Inorganic Chemistry", Prentice-Hall New York, 1944, p. 108.
28. Zhukov, J. Rus . Phys. Chem. Soc. 40, 457 (190); C.A. 3, 871 (1909)

[illegible] and [illegible] the formation of L_6, (vi) L_7. An investigation conducted by Tsuzuki [1] showed that the more stable the composition of the [illegible], and the greater the stable volume of the [illegible]. The figure is the decomposition temperature and consequently the more stable it is to the action of various reagents.

4. Luminous Substances.

From the chemical nature of phosphors particularly and energies activities are linked together in a closed form at 120°, a reviewed series of associate is formed, the [illegible] formation of which may be displayed to [illegible], there = 6, 4, 5, 6, 7 the higher [illegible] [147]. All members of this series seem to be [illegible] in stability. Due to [illegible] in [illegible] and [illegible], there the [illegible] have [illegible] [illegible] low melting points. This series of phosphors [illegible] [illegible] with [illegible] water. The [illegible] of [illegible] can be [illegible] by the addition of a little [illegible] to the water. Thus [illegible], these compounds yield [illegible] derivatives [illegible].

References.

1. Ayre and [illegible], J. [illegible]. [illegible] [illegible] (1931); G. A. [illegible] (1931).
2. [illegible] and [illegible], J. Chem. Soc., 77, [illegible] (1900).
3. [illegible], Chem. [illegible], [illegible], 120 ([illegible]).
4. [illegible], Ann. Chim. Phys., [illegible], 126 ([illegible]).
5. [illegible] and [illegible], Ber., [illegible], [illegible] (1904).
6. [illegible] and [illegible], [illegible], [illegible] (1910).
7. [illegible], J. Chem. Soc., [illegible], [illegible] ([illegible]).
8. [illegible], J. Am. Chem. Soc., [illegible], 580 ([illegible]).
9. [illegible] and [illegible], [illegible] Chem. Chem., [illegible], [illegible] ([illegible]); G. A. [illegible], 2[illegible] ([illegible]).
10. [illegible], Compt. rend., [illegible], [illegible] ([illegible]).
11. [illegible], J. physik. Chem., [illegible], [illegible] ([illegible]); G. A. [illegible], [illegible] ([illegible]).
12. [illegible], [illegible], [illegible], [illegible] ([illegible]).
13. [illegible], Compt. rend., [illegible], [illegible] ([illegible]).
14. [illegible] and [illegible], J. [illegible], [illegible], [illegible] ([illegible]); G. A. [illegible], [illegible] ([illegible]).
15. [illegible], [illegible], [illegible], [illegible] ([illegible]).
16. [illegible] and [illegible], [illegible], [illegible] ([illegible]); G. A. [illegible], [illegible] ([illegible]).
17. [illegible], Compt. rend., [illegible], [illegible] ([illegible]).
18. [illegible], J. Chem. Soc., [illegible], [illegible] ([illegible]).
19. [illegible], [illegible], [illegible], [illegible] ([illegible]).
20. [illegible], [illegible], [illegible], [illegible] ([illegible]).
21. [illegible], [illegible], [illegible], [illegible] ([illegible]).
22. [illegible], [illegible], [illegible], [illegible] ([illegible]).
23. [illegible], [illegible], [illegible], [illegible] ([illegible]).
24. [illegible], [illegible], [illegible], [illegible] ([illegible]).
25. [illegible], [illegible], [illegible], [illegible] ([illegible]).
26. [illegible], [illegible], [illegible], [illegible] ([illegible]).
27. [illegible], [illegible], [illegible], [illegible] ([illegible]).
28. [illegible], [illegible], [illegible], [illegible] ([illegible]).
29. [illegible], [illegible], [illegible], [illegible] ([illegible]).
30. [illegible], [illegible], [illegible], [illegible] ([illegible]).
31. [illegible], [illegible], [illegible], [illegible] ([illegible]).
32. [illegible], [illegible], [illegible], [illegible] ([illegible]).
33. [illegible], [illegible], [illegible], [illegible] ([illegible]).
34. [illegible], [illegible], [illegible], [illegible] ([illegible]).
35. [illegible], [illegible], [illegible], [illegible] ([illegible]).
36. [illegible], [illegible], [illegible], [illegible] ([illegible]).
37. [illegible], [illegible], [illegible], [illegible] ([illegible]).
38. [illegible], [illegible], [illegible], [illegible] ([illegible]).
39. [illegible], [illegible], [illegible], [illegible] ([illegible]).
40. [illegible], [illegible], [illegible], [illegible] ([illegible]).
41. [illegible], [illegible], [illegible], [illegible] ([illegible]).
42. [illegible], [illegible], [illegible], [illegible] ([illegible]).
43. [illegible], [illegible], [illegible], [illegible] ([illegible]).
44. [illegible], [illegible], [illegible], [illegible] ([illegible]).
45. [illegible], [illegible], [illegible], [illegible] ([illegible]).
46. [illegible], [illegible], [illegible], [illegible] ([illegible]).
47. [illegible], [illegible], [illegible], [illegible] ([illegible]).
48. [illegible], [illegible], [illegible], [illegible] ([illegible]).
49. [illegible], [illegible], [illegible], [illegible] ([illegible]).
50. [illegible], [illegible], [illegible], [illegible] ([illegible]).
51. [illegible], [illegible], [illegible], [illegible] ([illegible]).
52. [illegible], [illegible], [illegible], [illegible] ([illegible]).
53. [illegible], [illegible], [illegible], [illegible] ([illegible]).
54. [illegible], [illegible], [illegible], [illegible] ([illegible]).
55. [illegible], [illegible], [illegible], [illegible] ([illegible]).
56. [illegible], [illegible], [illegible], [illegible] ([illegible]).
57. [illegible], [illegible], [illegible], [illegible] ([illegible]).
58. [illegible], [illegible], [illegible], [illegible] ([illegible]).
59. [illegible], [illegible], [illegible], [illegible] ([illegible]).
60. [illegible], [illegible], [illegible], [illegible] ([illegible]).
61. [illegible], [illegible], [illegible], [illegible] ([illegible]).
62. [illegible], [illegible], [illegible], [illegible] ([illegible]).
63. [illegible], [illegible], [illegible], [illegible] ([illegible]).
64. [illegible], [illegible], [illegible], [illegible] ([illegible]).
65. [illegible], [illegible], [illegible], [illegible] ([illegible]).
66. [illegible], [illegible], [illegible], [illegible] ([illegible]).
67. [illegible], [illegible], [illegible], [illegible] ([illegible]).
68. [illegible], [illegible], [illegible], [illegible] ([illegible]).
69. [illegible], [illegible], [illegible], [illegible] ([illegible]).
70. [illegible], [illegible], [illegible], [illegible] ([illegible]).
71. [illegible], [illegible], [illegible], [illegible] ([illegible]).
72. [illegible], [illegible], [illegible], [illegible] ([illegible]).
73. [illegible], [illegible], [illegible], [illegible] ([illegible]).
74. [illegible], [illegible], [illegible], [illegible] ([illegible]).
75. [illegible], [illegible], [illegible], [illegible] ([illegible]).

ROLL CALL

January 23, 1945

Hydrides of Aluminum and Gallium — Therald Moeller

For many years the boron hydrides have been regarded as unique among the covalent hydrides because of lack of sufficient electrons for the formation of complete series of electron pair bonds. Recent reports of the preparation of a volatile gallium hydride, Ga_2H_6 (1, 2); and a non-volatile polymeric aluminum compound of composition $(AlH_3)_x$ (3) would indicate this phenomenon to be general among at least the beginning members of Periodic Group IIIb.

Preparation of the gallium compound (1, 2) involves reaction of $Ga(CH_3)_3$ with H_2 in a glow discharge to produce $Ga_2H_2(CH_3)_4$ which in turn reacts with $(C_2H_5)_3N$ to give $Ga(CH_3)_3.N(C_2H_5)_3$ and Ga_2H_6. The latter compound solidifies at -21.4°C. and boils, with decomposition, at 139°C.

Preparation of the aluminum compound (3) is similar in that it first involves the reaction of $Al_2(CH_3)_6$ with H_2 in a glow discharge. A complex mixture of volatile and non-volatile components results, from the volatile portion of which $Al_2H_2(CH_3)_4$ can be separated. Treatment of this material with $(CH_3)_3N$ yields $Al(CH_3)_3.N(CH_3)_3$ which, on heating, eventually gives $(AlH_3)_x$, a white, non-volatile solid, stable to 100°C., but decomposing at higher temperatures to Al and H_2.

References:

1. Wiberg and Johannsen: Naturwissenschaften 29, 320 (1941).
2. Wiberg and Johannsen: Die chemie 55, 38 (1942).
3. Stecher and Wiberg: Ber 75, 2003 (1942).

ROLL CALL

January 23, 1945

Report on the "Industrial and Electrochemical Conference" held in Chicago, January 19, 1945.

John C. Bailar, Jr.

This conference, sponsored by the Chicago section of the Electrochemical Society, was designed to convince businessmen of the possibilities for a postwar electrochemical industry in the midwest. The early talks dwelt on Chicago as a manufacturing center and on its power supply.

Dr. Harold Vagtborg, President of the Midwest Research Institute, predicted the growth of many such institutes to serve the smaller companies that can't economically have research laboratories of their own. According to him, there are less than 3000 companies in the United States which are doing research, although there are 180,000 which might well undertake research programs. Before the war, 0.5% of our national income was spent on research, but the Russians were spending 1% of their national income.

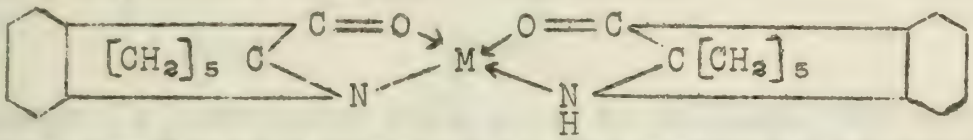
The outstanding talk of the conference was given by R. B. Wittenberg of the International Minerals and Chemical Corporation. He spoke of the five M's of the chemical industry -- management, money, men, markets, and materials -- and told of the importance of each in locating a new chemical industry. The first two are relatively unimportant in this regard. The chemical industries do not require a great quantity of labor, but the quality must be high, so new industries should be located where intelligent, educated labor is available. Markets and materials, of course, play a large role, and may well be determining factors. Even in an electrochemical industry, power may be of secondary importance.

This conference has been described in some detail in Chem. and Eng. News. 23, 238 (1945).

ADDITION COMPOUNDS OF THE ALKALI METALS AND THEIR STRUCTURES

Hans Jonassen February 20, 1945

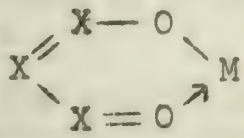
One of the outstanding properties of the alkali metals is their extremely slight tendency to form complex ions. One of the first coordination compounds of these metal ions is reported by Perkin and Plant (1) who isolated a sodium derivative of indoxylspiro cyclopentane. Sidgwick and Plant (2) continued this investigation of alkali complexes with indoxylspiro cyclopentane. They succeeded in isolating an unstable derivative with lithium and stable derivatives with sodium and potassium and assigned the following structure to these complexes:



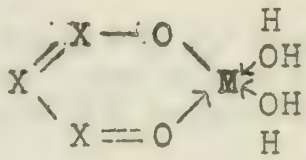
All these complexes decompose in the presence of excess water.

Sidgwick and Brewer (3) extended this work; they were able to prepare numerous solid alkali derivatives with organic molecules containing two electron donor groups. They divided these compounds into four groups with the following structures. X = C or N

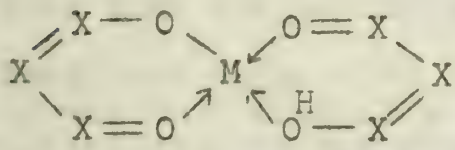
(I)



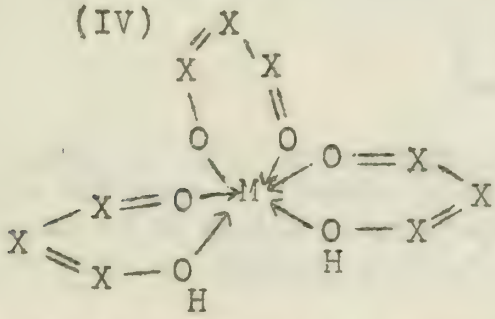
(III)



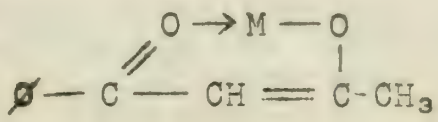
(II)



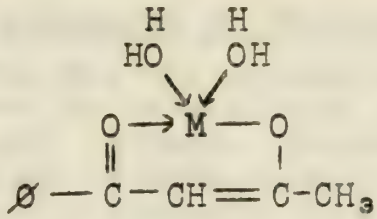
(IV)



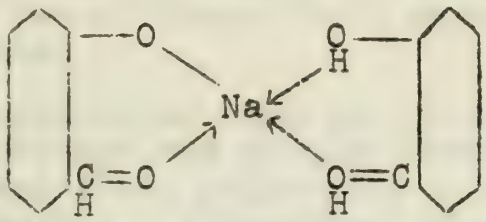
These authors state in their discussion that compounds having structure I are true salts since they show no definite melting points and since they are insoluble in nonhydroxylic solvents. A typical compound of this group is the sodium salt of benzoyl acetone:



Compounds having structures II, III, and IV are coordinate covalent compounds since they are soluble in organic solvents and show definite low melting points. Typical compounds of these groups are the dihydrated sodium salt of benzoyl acetone:



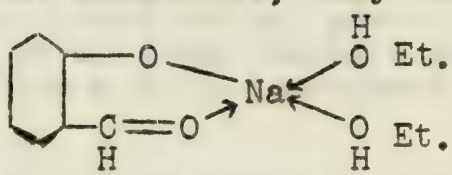
and the addition compound of sodium and two salicylaldehyde molecules



Brewer (4) extended this work to include the most active alkali metal ions cesium and rubidium. He prepared several new addition compounds of these ions with organic molecules, especially salicylaldehyde. In his conclusion Brewer gives a tabulation of all the important addition compounds of the alkali metal ions. The most important contribution of Brewer is that he was able to show that the coordination number of the alkali metals increases in these compounds as would be expected from the increase in their ionic sizes.

The addition compounds of β-alanine prepared by King and Rutherford (5) are of a slightly different type since in these complexes both the positive alkali ion and the negative ion add.

Brady and Badger (6), extending the work of Sidgwick, found that in absolute alcohol a compound is formed between sodium ion and salicylaldehyde and ethyl alcohol molecules; they tentatively assigned it the following formula:



In the course of dye investigations, Brady and Porter (7) were able to prepare extremely stable addition compounds of all the alkali metal ions with 4-isonitro-1-phenyl-3-methyl-5-pyrazolone. These compounds are extremely stable in water, soluble in organic solvents.

Hogson and Batty (8) continued this work and reported the isolation of sodium addition compounds with 2-nitroso-5-methoxyphenols and with some of their substituted derivatives.

During their investigations of the structures of di-2-hydroxy-1-naphthyl sulfide and the corresponding methane, Smiles and coworkers (9,10,11,12) were able to isolate hydrated alkali derivatives of these compounds. Due to its theoretical interest

this work was extended to include substituted benzenehydroxy sulfides and related compounds.

Discussion of Structure

In all these papers and the subsequent reviews (13, 14) these compounds are considered to be chelated inner complex compounds with coordinated covalent linkage. However, many experimental facts cannot be explained if such simple linkage is assumed. Most experimental facts seem to indicate that the linkage in these addition compounds is much more complex. They seem to indicate that the linkage in these compounds is ion dipolar rather than coordinate covalent. A few of these facts which seem to substantiate this are given below:

(1) Benzoylacetone does not form addition compounds with potassium, rubidium and cesium because their relatively large radii decrease their polarizing powers.

(2) Sodium and lithium form tetrahydrates with 2-di-hydroxy-1-naphthyl sulfide, selenide, and methane whereas potassium and rubidium only form dihydrates.

(3) In the benzene hydroxy sulfides alkali addition compounds are formed only when the 6 methyl group is present. Since the methyl group is an electron repelling group this increases the electron density in the 1 position. This, in turn, increases the attraction of this position for the hydroxylic proton, which then favors the ketonic form of the benzene hydroxy sulfide. If the alkali derivative formed were purely coordinate covalent it would make little difference whether the ketonic or enolic form were present, because in both cases unshared electrons are present in the outer orbit of the oxygen atom. If, however, ion dipolar linkage is involved the ketonic form should form a much more stable form because its dipole moment is much larger. There is, however, a further factor which has to be considered in the formation and stability of these compounds -- the size of the cation and the distances between the coordinating group in the molecule which adds. A consideration of these factors explains for example, why lithium does not form a stable compound with indoxyl spiro cyclopentane.

Sidgwick's statement that solubility in organic solvents is a criterion for covalency is not necesssrily valid. It can also be explained if a "lock and key" arrangement is assumed similar to that mentioned in Glasstone's article on intermolecular complexes (15). If such an arrangement is assumed, the inorganic part of the molecule would be completely hidden by the much larger organic molecules surrounding it. This explains also why compounds having structure I (cf. p. 53) are insoluble in organic solvents whereas compounds having the other structures are soluble.

The experimental facts discussed in the above part seem to indicate quite clearly that the linkage in the addition compounds of the alkali metal ions with organic molecules containing two electron donor groups is not as simple as maintained by Sidgwick.

Bibliography

1. Perkin and Plant, J. Chem. Soc. 123, 676, (1923).

2. Sidgwick and Plant, ibid. 127, 209 (1925).

3. Sidgwick and Brewer, ibid, 127, 2379 (1925).

4. Brew, ibid, 1931, 361.

5. King and Rutherford, ibid, 1931, 3131.

6. Brady and Badger, ibid, 1932, 952.

7. Brady and Porter, ibid, 1933, 840.

8. Hogson and Batty, ibid, 1935, 1617.

9. Evans and Smiles, ibid, 1937, 727.

10. Smiles and McClement, ibid, 1937, 1017.

11. Smiles and Shearing, ibid, 1937, 1933.

12. Smiles and Dvorkovitz, ibid, 1938, 2022.

13. Ann. Repts. Chem. Soc., 30, 88 (1933).

14. ibid., 35, 165 (1938).

15. Glasstone, Trans. Far. Soc., 33, 200 (1937).

ADSORPTION AND SURFACE IONIZATION ON TUNGSTEN

C. R. Keizer March 6, 1945

I. Introduction
  A. Definitions
    1. Adsorption--the process in which molecules or atoms of a gas or vapor become more or less firmly bound to the surface of a solid.
      a. adsorbent--the solid upon which the adsorption takes place.
      b. adsorbate--the gas which is adsorbed.
    2. surface ionization--the process in which molecules or atoms of a gas or vapor are ionized under the proper conditions upon contact with a solid surface.
  B. Properties of tungsten which account for its use as the most common adsorbent (1, 2, 3, 4)
    1. in powder form
      a. available in rather pure, uniform samples or easily prepared by reduction of the oxide
      b. high sintering temperature permits reduction and degassing at 750° without irreversible alteration of the surface structure.
    2. in the form of filaments or wires
      a. easily cleaned--heating electrically (flashing) to a very high temperature for a few seconds frees surface from all contamination and eliminates gases from interior.
      b. temperature may be easily measured
        1) current-voltage characteristics (5)
          lead-loss corrections (6)
        2) optical pyrometer (7)
      c. stable at high temperatures--can be heated in vacuum for considerable periods of time even at 3000° K., at which temperature all other substances vaporize.
      d. electron emission serves as a sensitive indicator of the presence of adsorbed films. (8)
      e. temperature may be easily and rapidly changed.
      f. chemical stability
      g. other properties not as directly applicable
        1) vacuum-tight seals to glass
        2) strength
        3) ductility
        4) connections to other metals

II. Adsorption (9, 10)
  A. Types of adsorption
    1. physical adsorption--weak interaction between solid and gas; essentially surface condensation; also called van der Waals, low temp. and secondary adsorption.
    2. chemical adsorption (chemisorption)--strong interaction between solid and gas; essentially surface reaction; also called activated, high temperature and primary adsorption.

B. Experimental Methods
  1. Measurement of amount of adsorption
    a. direct
      1) volumetric
      2) gravimetric
    b. indirect
      1) thermionic emission
      2) photoelectric emission
      3) reflection of polarized light
      4) accommodation coefficient
      5) contact potential
      6) electron diffraction
  2. Measurement of specific surface of adsorbent
    a. chemical
    b. physical
    c. optical
    d. electrical
  3. Measurement of heat of adsorption
  4. Presentation of data
    a. isotherm
    b. isobar
    c. isotere
C. Experimental Observations and Deductions
  1. on gases
    a. Langmuir and co-workers (8, 11, 12)
      1) used bulb method, W filament at 1500° K.
      2) hydrogen decomposed to H atoms, which were adsorbed on surface of bulb
      3) oxygen formed WO_3 which evaporated from filament
      4) with mixture of H and O, O disappeared first, then H. Oxide film prevented dissociation of hydrogen molecules.
      5) nitrogen and carbon monoxide formed films similar to oxygen and hydrogen films.
      6) second layer of gases adsorbed at higher pressures
      7) Condensation-Evaporation theory developed to explain these observations.
    b. Roberts (13, 14)
      1) used accomodation coefficient for Ne as measure of adsorption
      2) found filament immediately covered with film of H when exposed to the gas
      3) similar chemisorbed layer of oxygen, stable up to 1700°C. and second layer unstable above 60°
    c. Frankenburger and Hodler (15)
      1) isotherms for hydrogen, nitrogen and ammonia adsorption on W powder--each formed monolayer.
      2) in mixtures, adsorption uninfluenced by presence of other gases
      3) assumed imide and nitride formation as intermediates in decomposition of ammonia

d. Frankenburg (16)
1) studied hydrogen adsorption on W powder over wide range of temperature and pressure
2) found saturation only at high pressures
3) differential heats of adsorption calculated by Clausius-Clapeyron equation
4) at slight coverage H was assumed to be adsorbed as single H atoms; otherwise as molecules
5) heat of adsorption found to be sharply dependent on extent of coverage; explained by
a) heterogeneous nature of W surface
b) differences in state of adsorbed H.

1. for metals
a. Cs studied by Langmuir and associates (8, 12). These studies led to the recognition of the phenomenon of surface ionization.
b. Becker (17) also studied Cs and Ba and Th.
1) for Cs slight coverage at high temperatures.
2) more Cs adsorbed at lower temperatures.
3) thermionic emission a maximum with surface just covered with monatomic layer.
4) at still lower temperatures, still more Cs adsorbed but emission decreases.

D. Surface Migration--lateral motion of adsorbed molecules or atoms over the surface on which they have been adsorbed.
1. Bosworth (18) studied mobility of Na on W strip filament
a. measured photoelectric properties of surface
b. found limit to the capacity of the strip to adsorb Na.
c. excess Na stable on surface, spreads or migrates
d. strip becomes uniformly active in one or two hours at 300° K or 5-10 seconds at 800° K.
2. Becker (19) investigated Ba on W filament
a. measured thermionic emission
b. Ba deposited on one side of W strip, mounted as filament in thermionic valve
c. emission from bare side was found to increase; that from covered side found to decrease until rates were equal.

III. Surface Ionization
A. Metal vapors
1. first recognized by Kingdon and Langmuir (20) while studying the thermionic properties of W filaments coated with caesium; later (21) they found the extent of ionization to be dependent on the condition of the tungsten surface and developed a theory based on the Saha equation (22)
2. confirmatory and supplementary observations
a. Ives (23) Cs on W
b. Becker (17) Cs on W, W-O
c. Killian (24) Rb, K on W--like Cs
d. Meyer (25) K on W, Mo, Ta

e. Althertum, Krebs, and Rompe (26) studying Na and Cs on W, Re found that the temperature dependence of yield of Na^+ from W agreed with theory but yield of Cs^+ fell below theoretical value.

f. Morgulis (27) found that the yield of Na^+ agreed with theory at pressures in range 10^{-3} to 10^{-5} mm. Hg; at lower pressures secondary effects caused disagreement.

g. Mayer (28) studying K on Pt and W found yield of K^+ lower than that predicted by Langmuir-Saha theory.

3. studies at higher temperatures (up to 2700° K) using molecular beam method--Copley and Phipps (29, 30).

B. Metal halides

1. first observed by Rodebush and Henry (31).
2. Phipps and co-workers investigated positive ions
   a. KCl with Copley (32) and Hendricks and Copley (33)
   b. NaCl with Johnson (34)
   c. $BaCl_2$ with Arnett (35)
3. NaCl, KCl, and CsCl were studied by Dukelsky and Yonov (36), who were interested in the negative ions produced.

C. Halogens

1. Mayer with Sutton (37) studied iodine; with Mitchell (38) studied chlorine.
2. Yonov (39) has developed a theory, similar to that of Langmuir, for the case in which a halogen atom leaves the metal surfade as a negative ion.

IV. Applications

A. Theory of surface forces of solids.

B. Mechanism of heterogeneous catalysis (40, 41).

Bibliography

1. von Angerer, Technische Kunstgriffe bei physikalischen Untersuchungen, F. Vieweg und Sohn, Braunschweig, 1939. 4th Edition, pp. 14, 16, 52, 108, 123.
2. Strong, Procedures in Exoerimental Physics, Prentice-Hall, Inc., New York, 1942. pp. 23, 544.
3. Li and Wang, Tungsten, Reinhold Publ. Corp., New York, 1943.
4. Hopkins, General Chemistry, D. C. Heath and Co., Chicago, 1942. 3rd Edition, pp. 684-686.
5. Jones and Langmuir, Gen. Elec. Rev., 30, 310, 354 (1927).
6. Langmuir, MacLane, and Blodgett, Phys. Rev., 35, 478 (1930).
7. Forsythe and Worthing, Astrophys. J., 61, 146 (1925).
8. Langmuir, J. Chem. Soc., 1940, 511.

9. Brunauer, The Adsorption of Gases and Vapors, Vol. I (Physical Adsorption), Princeton Univ. Press, Princeton, N. J., 1943.
10. Smithells, Gases and Metals, J. Wiley and Sons, Inc., New York, 1937.
11. Langmuir, J. Am. Chem. Soc., 40, 1361 (1918).
12. Langmuir, Chem. Rev., 13, 147 (1933).
13. Roberts, Proc. Roy. Soc., 152A, 445, 477 (1935).
14. Roberts, Nature, 137, 659 (1936).
15. Frankenburger and Hodler, Trans. Faraday Soc., 28, 229 (1932).
16. Frankenburg, J. Am. Chem. Soc., 66, 1827, 1838 (1944).
17. Becker, Phys. Rev., 28, 341 (1926).
18. Bosworth, Proc. Roy. Soc., 150A, 58 (1935).
19. Becker, Trans. Faraday Soc., 28, 148 (1932).
20. Kingdon and Langmuir, Phys. Rev., 21, 380 (1923).
21. Langmuir and Kingdon, Proc. Roy. Soc., 107A, 61 (1925).
22. Saha, Phil. Mag., 40, 472, 809 (1920).
23. Ives, Phys. Rev., 21, 385 (1923).
24. Killian, Phys. Rev., 27, 578 (1926).
25. Meyer, Ann. Physic, 4, 357 (1930)
26. Althertum, Krebs, and Rompe, Z. Physik, 92, 1 (1934).
27. Morgulis, Physik. Z. Sowjetunion, 5, 221 (1934); J. Phys. Chem. (U.S.S.R.), 5, 236 (1934).
28. Mayer, Z. Physik, 105, 725 (1937).
29. Copley and Phipps, Phys. Rev., 45, 344 (1934).
30. Copley and Phipps, Phys. Rev., 48, 960 (1935).
31. Rodebush and Henry, Phys. Rev., 39, 386 (1932).
32. Copley and Phipps, J. Chem. Phys., 3, 594 (1935).
33. Hendricks, Phipps, and Copley, J. Chem. Phys., 5, 868 (1937).
34. Johnson and Phipps, J. Chem. Phys., 7, 1039 (1939).
35. Arnett, doctorate thesis, Urbana, Ill. (1941).
36. Dukelsky and Yonov, J. Exptl. Theor. Phys. (U.S.S.R.), 10, 1248 (1940).
37. Sutton and Mayer, J. Chem. Phys., 3, 20 (1935).
38. Mitchell and Mayer, J. Chem. Phys., 8, 282 (1940).
39. Yonov, Compt. rend. acad. sci. (U.S.S.R.) "Doklady", 28, 512 (1940).
40. Griffith, The Mechanism of Contact Catalysis, Oxford Univ. Press, London, 1936.
41. Taylor, Twelfth Report of the Committee on Catalysis, J. Wiley and Sons., Inc., New York, 1940. Chapters III, IV.

THE STRUCTURE OF LIQUIDS

W. E. Morrell March 13, 1945

What is the arrangement of molecules in a liquid? Is it random, as in gases? Does it resemble the ordered arrangement found in crystals, being either microcrystalline (containing tiny but almost perfect crystals) or quasicrystalline?

The simplest approach to the problem is through the consideration of pure liquids composed of non-polar and practically spherical molecules. Such an approach avoids problems of orientation, whether caused by the shapes of the molecules themselves or by dipoles, and avoids the complications that would accompany the presence of more than one species of molecule.

The structure of a liquid containing a single species of spherical, non-polar molecule can be expressed in terms of a probability or distribution function W (often called g(r) or $\rho(r)$). W "is a measure of the statistical density of molecules at a distance r from any given molecule". $4\pi r^2 W\,dr$ "is hence the probability of finding a molecule within a distance r to r + dr of a given molecule" (4), or it is the average number of molecules around the reference molecule in a spherical shell of radius r and thickness dr. The total number of molecules within distance r of the reference molecule is therefore $4\pi \int_0^r Wr^2 dr$

"The distribution function uniquely characterizes the molecular configuration of a liquid" (4). All that remains to be done is the evaluation of W, the distribution function.

Several methods of evaluationshave been tried. A general idea of the way W varies with r can be obtained intuitively. Mathematical derivations are difficult, and have, in general, yielded only approximate results (1-9).

Experimental evaluations have in general involved (1) x-ray diffraction, or (2) the use of models.

The first satisfactory evaluation of the distribution function were obtained by means of x-ray diffractions in mercury, gallium, and CCl_4 by Debye and Menke (16). Their calculations are based on equations derived by Zernike and Prins (15).

Various kinds of models have been used. Menke (17) poured steel spheres repeatedly onto a flat plate, and measured and tabulated the distances between two black spheres. Prins (10) poured seeds onto a glass plate, photographed them, and from measurements obtained from the photographs, tabulated the relative frequencies of occurrence of the various distances between seeds.

Morrell and Hildebrand (11) used three dimensions instead of two by photographing solid gelatin spheres suspended in a liquid gelatin medium and thereby duplicated Menke's curve for mercury. (Therefore, the atoms in mercury are arranged much like oranges in a pile haphazardly dumped into a grocer's store window. The oranges in the pile show somewhat more regularity or order than do the atoms in mercury, however, as the weight and lack of motion of the oranges causes them to pack relatively more tightly). Stuart and Kast (12,13,14) went back to two dimensions and photographed small discs shaken on a glass plate. They added the effect of dipoles by attaching magnets to the discs.

While the use of models has been helpful, the most fruitful approach is now through the diffraction of x-rays. By this means, the distribution functions of quite a number of liquids have been obtained (15-26). It has been shown that twelve atoms are adjacent to each atom in liquid mercury (16,17), but in liquid potassium each atom is directly surrounded by only eight (22). Lead and bismuth, although they differ in crystal structures, have identical liquid structures (20). Neighboring plate-shaped molecules (e.g. benzene) tend to have flat sides parallel (26).

Long molecules (e.g. hydrocarbon chains) tend to form "cybotactic" groups, small groups of molecules with similar orientation. (Many references by G. W. Stewart and coworkers.)

The hydrogen-bonded, sponge or net-work like structure of water is now, of course, well known, and was elucidated by aid of x-ray diffraction measurements (18,23).

REFERENCES

Mathematical

1. Kirkwood, J. Chem. Phys. 3, 300-13 (1935).
2. Kirkwood, J. Chem. Phys. 7, 919-25 (1939).
3. Kirkwood and Boggs, J. Chem. Phys. 10, 394-402 (1942).
4. Bernal, Trans. Faraday Soc., 33, 27-45 (1937).
5. Prins and Petersen, Physica, 3, 147-53 (1936).
6. de Boer and Michels, Physica 6, 97-114 (1939).
7. Coulson and Rushbrooke, Phys. Rev. 56, 1216-23 (1939).
8. Corner, Proc. Phys. Soc. (London) 52, 764-7 (1940).
9. Corner and Lennard-Jones, Proc. Roy. Soc. (London) A178, 401-14 (1941).

Models

10. Prins, Naturwiss., 19, 435 (1931).
11. Morrell and Hildebrand, J. Chem. Phys. 4, 224-7 (1936)
12. Kast and Stuart, Physik. Z. 40, 714-18 (1939)
13. Stuart, Z. Electrochem. 47, 110-12 (1941)
14. Stuart, Kolloid Z. 96, 149-60 (1941)

X-Ray Diffraction

15. Zernike and Prins, Zeits. f. Physik. 41, 184-94 (1927).
16. Debye and Menke, Fortschr. d. Tech. Röntgenkunde, II, (1931).
17. Menke, Physik. Zeits., 33, 593-604 (1932).
18. Bernal and Fowler, J. Chem. Phys., 1, 515-548 (1933).
19. Randall, Trans. Faraday Soc., 33, 105-109 (1937).
20. Randall and Rooksby, Trans. Faraday Soc., 33, 109-10 (1937)
21. Trimble and Gingrich, Phys. Rev., 53, 278 (1938).
22. Thomas and Gingrich, J. Chem. Phys., 6, 411-15 (1938).
23. Morgan and Warren, J. Chem. Phys., 6, 666-673 (1938).
24. Barnes, Chem. Rev. 23, 29-43 (1938).
25. Gamertsfelder, J. Chem. Phys., 9, 450-457 (1941)
26. Bell and Davey, J. Chem. Phys. 9, 441-50; 450-57 (1941).

Reviews

27. Herzfeld, J. Applied Phys. 8, 319-27 (1937).
28. Warren, J. Applied Phys. 8, 645-54 (1937).
29. Fischer, Physik regelmässig. Ber. 8, 113-26 (1940).
30. Lennard-Jones, Proc. Phys. Soc. (London), 52, 729-47 (1940)
31. Kirkwood, Am. Scientist, 30, 191-201 (1942).

Miscellaneous

32. Hildebrand and Wood, J. Chem. Phys., 1, 817-22 (1933).
33. Hildebrand, Science 90, 1-8 (1939).
34. J. T. Randall, "Diffraction of X-Rays and Electrons by Amorphous Solids, Liquids and Gases", London, Chapman and Hall, 1934.
35. Volume 33 (1937) of the Transactions of the Faraday Society contains many papers presented at a symposium on "Structure and Molecular Forces in Pure Liquids and Solutions".

INORGANIC BENZENE

(Egon Wiberg, University of Munich)

T. G. Klose March 20, 1945

I. Introduction

The compound $B_3N_3H_6$ has been named triborine triamine, borazol and "inorganic benzene".

Stock and Pohland were the first authors to mention borazol and to study its properties to any extent. Their preparative method is still in use and gives a good yield of the compound.

$$B_2H_6 + 2NH_3 \xrightarrow[\text{sealed tube}]{200^\circ} 2BNH_2 + 4H_2$$

The compound was shown by the vapor density method to consist of three empirical units, thus giving the formula $B_3N_3H_6$. Stock and Pohland also showed that the compound was quantitatively hydrolyzed by hydrochloric acid:

$$B_3N_3H_6 + 9H_2O \longrightarrow 3H_3BO_3 + 2NH_3 + 3H_2$$

The greatest yield of "inorganic benzene" thus far reported is 41%, which was obtained by heating ammonia and diborane in the theoretical ratio of 2:1 for forty-five minutes.

II. Constitution of $B_3N_3H_6$.

This compound may have any one of several hundred possible formulas with straight and branched chains or rings. Structures containing the B-B bond are eliminated since they would be too unstable to meet the physical properties of inorganic benzene. This limits the compounds with an empirical formula of $B_3N_3H_6$ to less than a dozen.

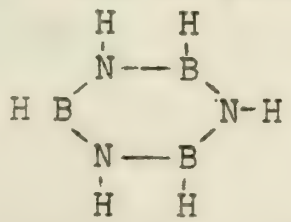
The decision as to the correct formula was made by studies on the two trimethyl substitution products of inorganic benzene $B_3(CH_3)_3N_3H_3$ and $B_3N_3(CH_3)_3H_3$. Most of the trimethyl substitution products have been prepared by Schlesinger, Horvitz and Burg who suggested a mechanism for their formation.

A hydrogen atom was found to be attached to each boron and nitrogen atom by a study of the hydrolysis of the isomeric trimethyl benzenes:

$$B_3N_3(CH_3)_3H_3 + 9HOH \longrightarrow 3B(OH)_3 + 3NH_2CH_3 + 3H_2$$

and $$B_3(CH_3)N_3H_3 + 6HOH \longrightarrow 3CH_3B(OH)_2 + 3NH_3$$

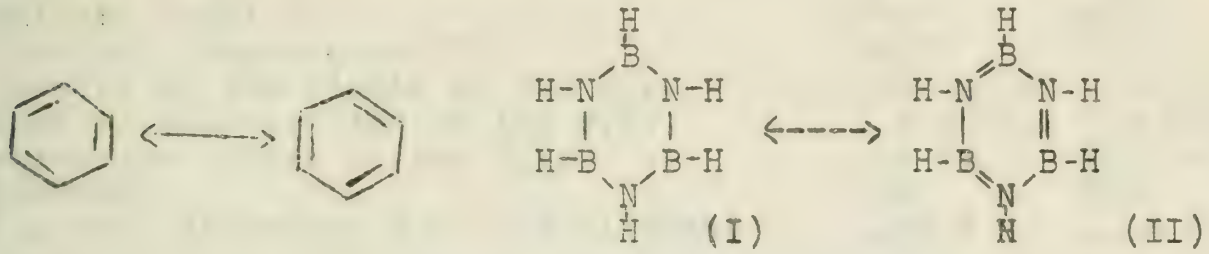
The only structural formula which is possible in light of these hydrolytic properties is:



Stock and Pohland have pointed out that such a "benzene formula" is consistant with all the experimental observations.

Bauer has made diffraction patterns of $B_3N_3H_6$ and found them to correspond almost exactly with diffraction patterns of benzene.

The borazol molecule may exist in one of two possible forms or it may resonate; as with benzene:

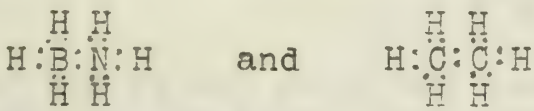


Wiberg reports that the calculated parachor for molecule (I) would be 195 and the calculated value for (II) 260. The experimental value was found to be 208. It thus appears to be in resonance forms.

There are other cases besides "inorganic benzene" in which the C-C pair is substituted with the B-N pair with a remarkable retention of chemical and physical properties.

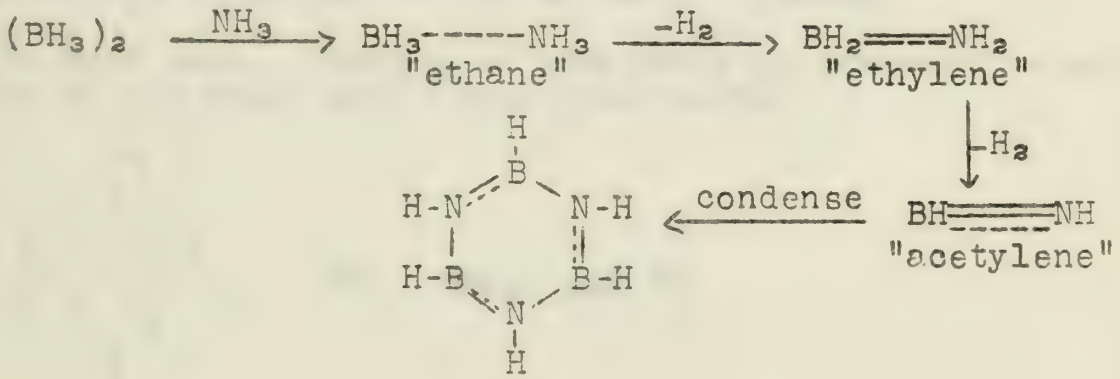
Boron nitride ("inorganic graphite") is analogous to graphite. In fact, two adjacent C-atoms may be replaced with B-N without changing the atomic distances in the lattice.

Ethane and BH_3NH_3 show a close similarity also, as could be predicted from their electronic configurations:



II. Mechanism.

Wiberg's suggested mechanism:



IV. Physical Properties.

Inorganic benzene, like benzene, is a colorless, mobile, inflammable liquid with good solvent properties and a characteristic aromatic order.

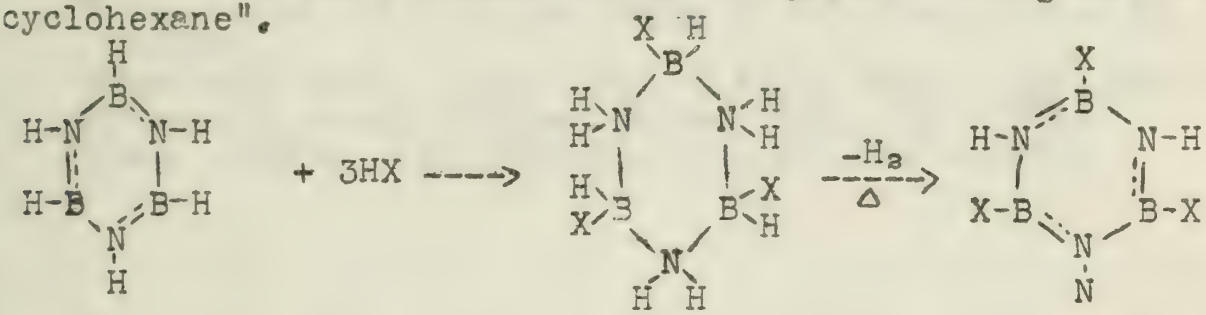
Summary of Properties

	Organic Benzene	Inorganic Benzene
Molecular weight	78	80
Boiling point K°	353°	328°
Melting point K°	279°	215°
Critical Temperature K°	561°	525°
Density of the liquid at the B.P.	.81 g/cc	.81 g/cc.
Heat of vaporization at the B.P.	7.4 Kcal.	7.0 Kcal
Molecular volume at the B.P.	96 cc.	100 cc.
Parachor	206	208
C<----->C distance; B<----->N distance	1.42 Å	1.44 Å

V. Chemical properties.

Inorganic benzene is slowly hydrolyzed at room temperature. A fresh solution of the compound acts as a reducing agent on such ions as MnO_4^- and Cu^{++}.

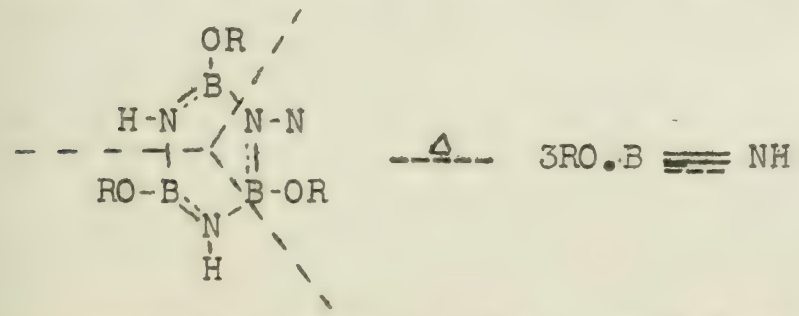
Three moles of a compound of the formula HX (HCl, HBr, HOH, $HOCH_3$) add to the 3 double bonds in $B_3N_3H_6$ forming an "inorganic cyclohexane".



This reaction is not rapid and doesn't appear to be salt formation between HX and the imino group -NH-.

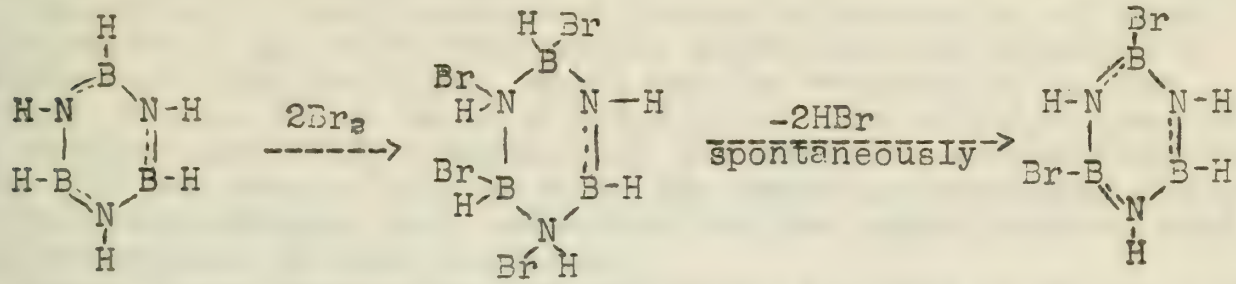
Heating the "cyclohexane" at 50-100° causes the splitting out of H_2 and the formation of the aromatic system.

In some cases, heating of the addition compound causes fission of the ring into three equal parts:



Catalytic hydrogenation of $B_3N_3H_6$ failed to yield a "hexahydrobenzol".

Bromination of "inorganic benzene" leads to the "m-dibromo benzene" whereas with C_6H_6, the p-dibromo compound results:



The hydrolysis product of the dibromo compound is volatile with steam and is thought to be "inorganic resorcinal".

BIBLIOGRAPHY

Stock and Pohland, Ber., 59, 2215 (1926).
Wiberg, Ber., 73, 299 (1940).
Bauer, J. Am. Chem. Soc., 60, 524 (1938).
Schlesinger, Horvitz and Burg, J. Am. Chem. Soc., 58, 409 (1936).
Stock and Wierl, Z. anorgan. allgem. Chem., 203, 228 (1931).
Wiberg, Z. anorg. allgem. Chem., 173, 199 (1928).
Stock, Wiberg, and Martini, Ber. 63, 2927 (1930).

ROLL CALL

March 27, 1945

ehavior of Metals in Nitric Acid

C. R. Keizer

According to electrochemical theory of corrosion of metals the anodic reaction is relatively simple involving the passage of metallic ions into solution, which may be represented by the equation $M \longrightarrow M^{n+} + ne$ ($n = 1,2,3...$). The cathodic reaction is more complex involving reduction of the reagent surrounding the metal. In the case of nitric acid two reactions are most probable, one yielding hydrogen upon reduction and the other nitrous acid, which decomposes in acid solution.

There is evidence that the reduction of nitric acid to nitrous acid is autocatalytic. Three possible steps in reduction of nitric acid are these:

(1) $HNO_3 + H^+ + e \longrightarrow NO_2 + H_2O$
(2) $NO_2 + H^+ + e \longrightarrow HNO_2$
(3) $HNO_2 + H^+ + e \longrightarrow NO + H_2O$
(1a) $NO_3^- + 2H^+ + e \longrightarrow NO_2 + H_2O$
(2a) $NO_2 + e \longrightarrow NO_2^-$
(3a) $NO_2^- + 2H^+ + e \longrightarrow NO + H_2O$

The author considers (2a) a very probable reaction since it involves only two particles. One British chemist thinks that NO_3^- and NO_2^- are not powerful oxidizing agents but that HNO_3 and HNO_2 are; this would favor (1) and (3) over (1a) and (3a). HNO_2 produced by (2) or (2a) rapidly regenerates NO_2 by the reaction

(4) $HNO_2 + HNO_3 \longrightarrow 2NO_2 + H_2O$

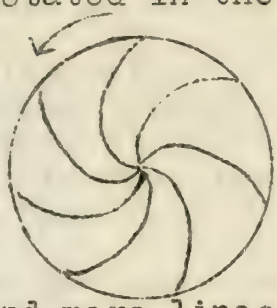
Once a trace of NO_2 has been formed, the reduction of HNO_3 proceeds more and more rapidly.

Highly reactive metals such as Mg, Zn, or Cd generally produce hydrogen or compounds containing it (NH_3, NH_2OH, N_2H_4). In this case the anodic attack is sufficiently rapid to produce a cathodic current density capable of maintaining the formation of hydrogen.

With noble metals (Ag, Cu) the reduction produces nitrous acid (eventually NO or NO_2). It has been found that the presence of urea in the solution represses the attack of the metal. This is explained by the fact that urea reacts with nitrous acid. On the other hand, urea was found to have no effect on the attack of Mg. It has been observed that the attack of HNO_3 on noble metals is most rapid at cracks and crevices where HNO_2 could accumulate. Stirring was found to slow down the action presumably because of removal of HNO_2 from the surface of the metal.

Rotation of a metal disc in HNO_3 was found to increase the rate of solution of Sn, Zn, Mg but to decrease the rate for Ag, Cu. Urmanczy obtained some interesting results when he rotated discs of Ag, Cu, and Zn in HNO_3 solution. For Ag he found that with HNO_3 of concentration less than 4M no weighable amount of Ag was dissolved in 20 minutes, the sample being rotated 220 x per minute. With increasing concentration of HNO_3 the Ag dissolved more and more rapidly. Slower rotation was found to increase the rate of solution of Ag.

Upon examination of the metal discs after being rotated in the HNO_3 he found unique patterns. These he interpreted as indicating that the rate of solution of Ag in HNO_3 is affected by the presence of NO_2. As the bubbles of NO_2 are formed they move out toward the edge of the disc due to centrifugal force. In passing along the surface of the metal they accelerate corrosion at each spot momentarily. These lines were found to be always bent according to the direction of turning the disc. At a higher rate of rotation he found more lines but they were not as deep as those found with lower rates of rotation. This is explained by the fact that the gas is not removed as rapidly when the disc is rotated more slowly.



Copper was found to give patterns similar to those obtained with silver. With zinc no lines were found -- which might be expected. The Zn being very reactive dissolves very rapidly and the catalytic effect of HNO_2 or NO_2 would not be noticeable.

References
U. R. Evans, Trans. Faraday Soc., 40, 120 (1944).
A. Urmanczy, Z. Anorg. Chem., 235, 363 (1938).

ROLL CALL H. A. Laitinen

I. Removal of oxygen from commercial tank nitrogen.

A. The common method of passing the nitrogen over copper turnings or gauze heated to temperature of 450-600° is limited in efficacy by the thermal decomposition of cupric oxide. The use of activated copper dispersed on fuller's earth is superior, since a temperature of 200-250° can be used. Finely dispersed copper oxide is prepared by dissolving basic copper carbonate in concentrated ammonium hydroxide, suspending the fuller's earth in the solution, evaporating to dryness and heating to 180°. The copper oxide is reduced by hydrogen at 200-250°.

Reference: Meyer and Rouge, angew Chem. 52, 637 (1939).

B. Chromous chloride solution can be used for the efficient absorption of oxygen. Lightly amalgamated zinc in a hydrochloric acid solution keeps the chromium reduced to the chromous condition.

II. Sensitive Methods for Analysis of Oxygen in Gases.

A. Probably the most sensitive method known is based on the measurement of phosphorescence which is caused by the presence of oxygen.

Reference: Pollack, Pringsheim and Terwoord, J. Chem. Phys. 12, 295 (1944).

B. The Pauling meter, based on the paramagnetism of molecular oxygen, has not yet been commercially perfected although it has been under development for some time.

C. An electrolysis method based on diffusion of oxygen through a porous graphite cathode is being commercially developed. The oxygen depolarizes the cathode and an electrolytic current proportional to oxygen content of the diffusing gas mixture is observed.

ROLL CALL

A NEW PERIODIC TABLE

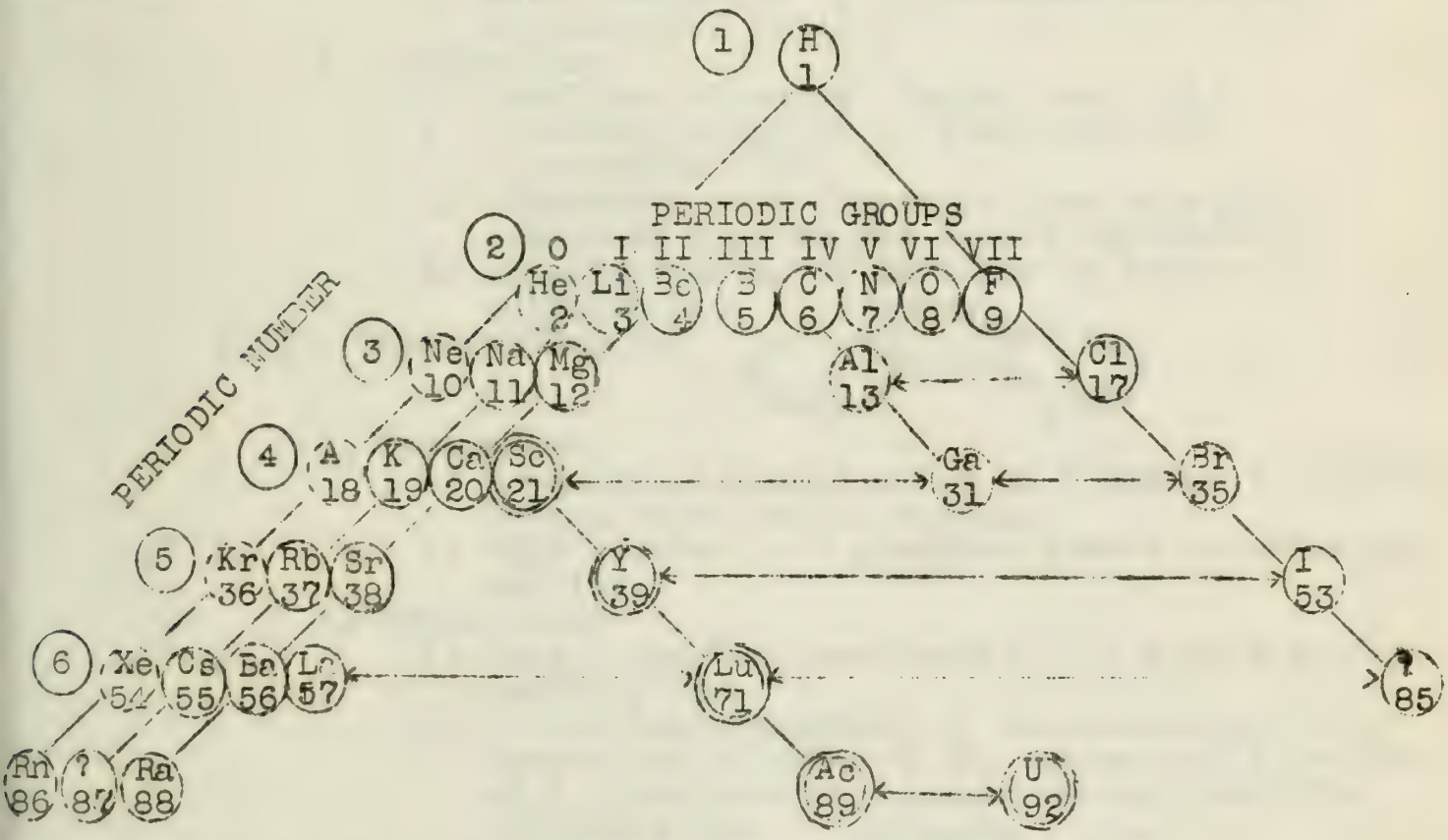
Donald R. Martin

The new table is simply a different geometric configuration of the Bohr table. Hydrogen is made the apex of an isosceles triangle, one side of which is the alkali metal family and the other side the halogen family. Thus the relationship of hydrogen to both families is shown. By such a configuration all the rare earths then fall into their regular position in the 6th series.

The four different types of elements as classified by Bohr are shown by different types of circles around the elements.

The electronic configuration of, Werner's coordination number of, the minimum and maximum valence exhibited by, the elements are also included in the table.

The abbreviated table below shows the general configuration of the table:



Electrons in Quantum Groups

Periods	K L M N O P Q
1	Z
2	2 Z
3	2 8 Z
4	2 8 Y Z
5	2 8 18 Y Z
6	2 8 18 X Y Z
7	2 8 18 32 X Y Z

Types of Elements

All groups Complete	2 Groups Incomplete
1 Group Incomplete	3 Groups Incomplete

Sloping Lines Represent Degrees of Similarity

————————	Very close similarity
———— ————	Close similarity
— — — — — —	Some similarity

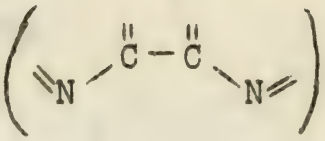
Wagner, H. A. and Booth, H. S., J. Chem. Ed. 22, 128-9 (1945).

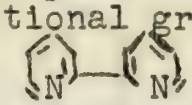
COORDINATION COMPLEXES OF DIPYRIDYL AND RELATED SUBSTANCES

F. W. Cagle April 3, 1945

I. Coordinating Agents

A. Pyridine (functional group )

B. Compounds with the functional group 

1. 2, 2'-bipyridyl 

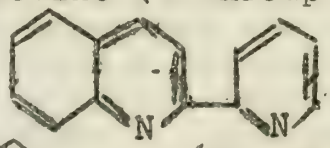
   a. Derivatives
      1) Substitution in the 3, 3' position destroys coordination ability.
      2) Substitution in 6 position reduces coordination ability.
      3) Substitution in 6, 6' position destroys coordination ability.

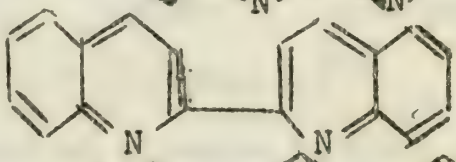
   b. Preparation
      1) Pyrolysis of copper 2-picolinate (1).
      2) Decarboxylation of 3, 3'-dicarboxy-2, 2' bipyridyl (2).
      3) Condensation of 2-brompyridine by ethyl magnesium bromide and cobalt chloride (3).
      4) Dehydrogenation of pyridine by ferric chloride (4).

2. 1, 10-phenanthroline 

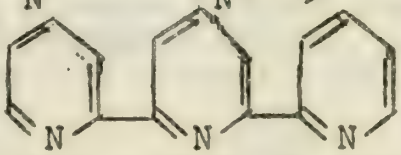
   a. Derivatives
      1) Products of substitution in 5 and/or 6 position retain coordination ability.
      2) Substitution in 3 position lowers coordination ability.

   b. Preparation
      1) From 1, 2-phenylenediamine by a double Skroup reaction (5).
      2) By the transformation of 2-nitroaniline into 8-amino-quinoline and the subsequent formation of 1, 10-phenanthroline (2 Skroup reactions involved) (6).

3. 2-(2' pyridyl)-quinoline  (7)

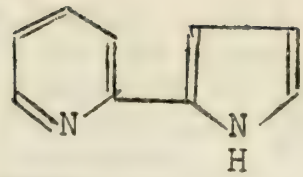
4. 2, 2'-biquinolyl  (7)

C. Miscellaneous related compounds.

1. 2, 2', 2"-terpyridyl 

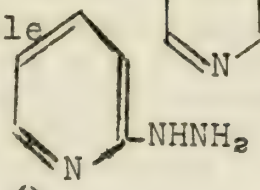
   (a byproduct from the preparation of 2, 2'-bipyridyl by dehydrogenation of pyridine)

2. 2-(2' pyridyl)-pyrrole



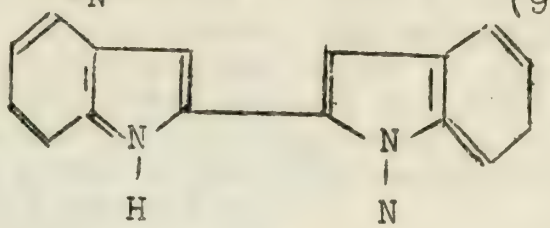
(8)

3. 2-pyridylhydrazine



(9)

4. 2, 2'-bi-indoyl



(10)

II. Complex Compounds

A. Complexes with pyridine involving simple coordinate bonds.

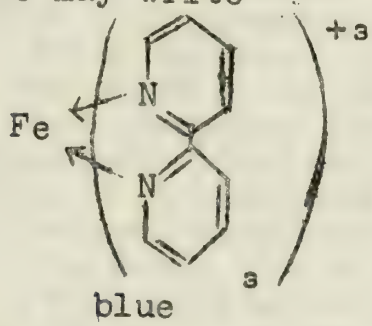
1. Some of these are $[Fe(Py)_4](SCN)_2$, $[Cd(Py)_2(SCN)_2]$, and $[Co(Py)_4](SCN)_2$.
2. Such compounds have been used for the determination of Cu^{+2}(11), Ni^{+2}(12), Cd^{+2}(13), Co^{+2}(14).

B. Pyridine complexes of a chelate nature.

1. Complexes with iron.

a. With 2, 2'-bipyridyl

Ferrous iron forms a bright red complex (15). We may write



$$+ e^- = \underset{\text{red}}{\left[Fe(bipy)_3\right]^{++}}$$

E (formal)(16) = 0.97V

bipy = 2,2'-bipyridyl

This bright red complex is often employed for the colorimetric determination of iron (17).

b. With 1, 10-phenanthroline and its substituted products.

Ferrous iron forms red complexes with these compounds (5). These compounds are used in the qualitative and quantitative determination of iron (18,19), and as oxidation-reduction indicators (20). phen = 1, 10-phenanthroline.

$$\underset{\text{blue}}{\left[Fe(phen)_3\right]^{+3}} + e = \underset{\text{red}}{\left[Fe(phen)_3\right]^{+2}} \qquad E(f) = 1.06 \text{ (21)}$$

For other members we observe similar reactions with the following E (formal) values.

Indicator as $FeSO_4$ Complex	E (formal) volts (21)
5-Nitro-phen	1.25
5-Methyl-6 Nitro-phen	1.23
5-Bromo-phen	1.12
5-Chloro-phen	1.12
5-Methyl-phen	1.02

c. With 2,2',2"-terpyridyl
Ferrous iron gives a reddish purple compound (22). No value for the E(f) can be given. This reagent is superior for small amounts of iron. The ferrous complex has the formula, $[Fe(terpy)_2]^{+2}$.

d. Complex with 2-pyridylhydrazine
Ferrous iron forms a purple complex with this reagent. The structure of this is in question (23,24,25). In any event, the material is never employed to estimate iron since it does not conform with the Beer-Lambert law (25).

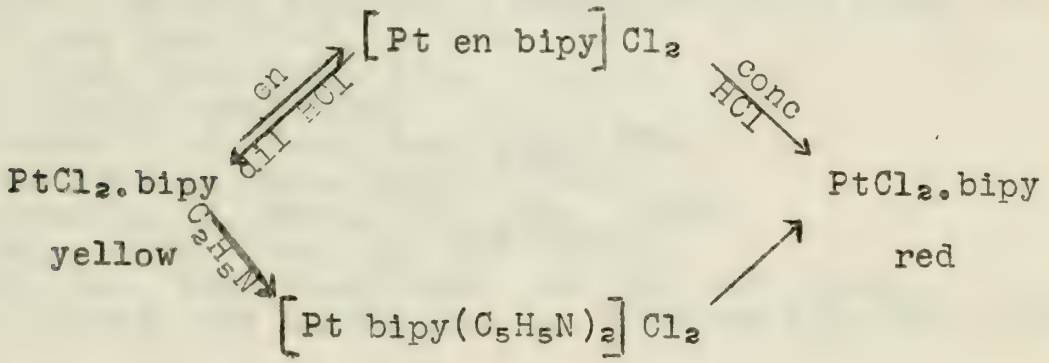
e. Complex with 2-(2' pyridyl)-pyrrole
Ferrous iron gives a reaction completely analogous to that in (d) above (26).

f. With 2-(2' pyridyl)-quinoline
A red color is produced with Fe^{+2} (27). The Fe^{+3} form is not described and the E(f) for the couple is unknown. There is some question concerning the ferrous complex (25).

2. Complexes with ruthenium
a. With 2, 2'-bipyridyl.
A bright red complex of the formula, $[Ru(bipy)_3]\ Cl_2.6H_2O$, may be prepared (28). This results from heating 2, 2'-bipyridyl and $RuCl_2$ together.

b. With 1,10 phenanthroline.
A red compound of presumably the same structure as that given for the dipyridyl analogue has been prepared (29).

3. Complexes with platinum
a. With 2, 2'-bipyridyl.
Several complexes of this type are known but the one which has received the most attention is $PtCl_2$.bipy which exists in anomalous isomers (30,31).



b. Complexes with 2, 2', 2"-terpyridyl.
A situation entirely analogous to that with 2, 2'-bipyridyl is found here (32).

4. Complexes with copper.
a. With 1, 10-phenanthroline
A brown cuprous compound of unknown composition is formed. This has been used for the colorimetric estimation of traces of copper (33, 34).

b. With 2, 2'-biquinolyl
A compound similar to that in (a) above is formed and has been used for the determination of copper (35).

References.

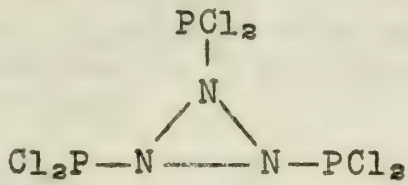
1. Blau, Ber. 21, 1077 (1888).
2. Wibaut and Willink, Rec. trav. Chim. 50, 287 (1931).
3. Smith and Richter, Phenanthroline and Substituted Phenanthroline Indicators, G. Fredric Smith Chemical Co.: Columbus, Ohio, 1944. p. 19-21.
4. Morgan and Burstall, J. Chem. Soc. (1932) 20.
5. Blau, Monatsh. 19, 666 (1898).
6. Smith, J. Am. Chem. Soc. 52, 397 (1930).
7. Smirnoff, Helv. Chim. Acta. 4, 802 (1921).
8. Emmert, Ber. 60, 2011 (1927); 62, 1733 (1929); 66, 1971 (1933).
9. Tachilschibabin and Rasovenow, Chem. Zentr. (1916) II, 16.
10. Smith and Richter, op. Cit. p. 16.
11. Spacu and Dick, Z. anal. Chem. 71, 185 (1927).
12. Spacu and Dick, Z. anal. Chem. 71, 442 (1927).
13. Spacu and Dick, Z. anal. Chem. 73, 279 (1928).
14. Spacu and Dick, Z. anal. Chem. 71, 97 (1927).
15. Blau, Monatsh. 10, 375 (1889).
16. Smith, Trans. Ill. Acad. Sci. 36, 132 (1943).
17. Hill, Proc. Roy, Loc. London (B), 107, 208 (1930).
18. Geigl, Chem. Ztg. 44, 689 (1920).
19. Saywell and Willard, Ind. Eng. Chem. Anal. Ed. 10, 13 (1938).
20. Walden, Hammett, and Edmonds, J. Am. Chem. Soc. 56, 350 (1934).
21. Smith and Richter, Ind. Eng. Chem. Anal. Ed. 16, 580 (1944).
22. Morgan and Burstall, J. Chem. Soc. 1932, 20.
23. Mellan, I., "Organic Reagents in Inorganic Analysis", The Blakiston Company: Philadelphia, 1941, p. 6.
24. Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry", D. Van Nostrand Company, Inc.: New York, 1942, p. 153.
25. Moss, M. L., Ph.D. Thesis, Purdue University (1942).
26. Emmert and Brandt, Ber. 60, 2211 (1927).
27. Yoe and Sarver, "Organic Analytical Reagents", John Wiley and Sons, Inc.: New York, 1941, p. 164.
28. Burstall, J. Chem. Soc. 1936, 173.
29. Smith, G. F., Unpublished work.
30. Morgan and Burstall, J. Chem. Soc. 1934, 965.
31. Rosemblatt and Scheede, Ann. 505, 58 (1935)
32. Morgan and Burstall, J. Chem. Soc. 1934, 1498.
33. Tartarini, Gazz. chim. ital. 63, 597 (1933).
34. Moss and Mell, Ind. Eng. Chem. Anal. Ed. 15, 116 (1943).
35. Breckenridge, Lewis, and Quick, Can. J. Research 17B, 258 (1939).

PHOSPHONITRILIC CHLORIDES AND "INORGANIC RUBBER"

L. J. Edwards March 29, 1945

It was shown by Liebig (6) in 1832 that when phosphorus pentachloride is treated with dry ammonia and the product heated, a white stable material is obtained to which Laurent (5) assigned the empirical formula $PNCl_2$. On the basis of vapour density studies Gladstone and Holmes (4) represented the compound as $(PNCl_2)_3$. It has since been realized that the trimer is the lowest member of the series of polymers.

Numerous disagreements have arisen concerning the structure of these polymers and several postulations were made to account for their physical and chemical properties. Because of the stability of these compounds towards heat and hydrolyzing agents, as well as the requirements of valency, cyclic formulae have been assigned to the halonitrides in which the rings are composed either of $>N-PCl_2$ or of $\geqslant N$ and $\geqslant PCl_2$ alternately (11, 12). Wichelhaus suggested the following cyclic formula for the trimer:

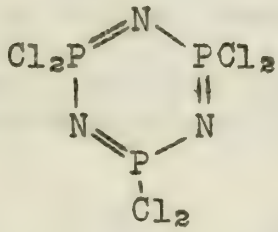


(I)

After an extensive study of the hydrolysis of the trimer, Stokes (11) thoroughly disagreed with this structure, stating that since,

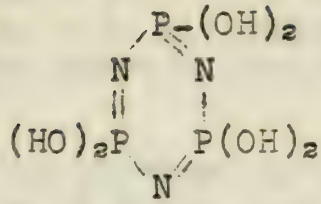
1) the compound decomposes into orthophosphoric acid and ammonia,
2) it is formed from ammonia and phosphorus pentachloride,
3) there are no indications of double or triple linked phosphoric acids or of hydrzine in the decomposition products,

it is probable that the phosphorus atoms are united by nitrogen atoms. Therefore, he agreed with the structure:



(II)

If this series of phosphonitrilic chlorides is considered to be made up of acid chlorides analogous to $POCl_3$, and if formula II is assumed to be the correct structural representation of the trimer, then hydrolysis should yield triphosphonitrilic acid corresponding to the form:



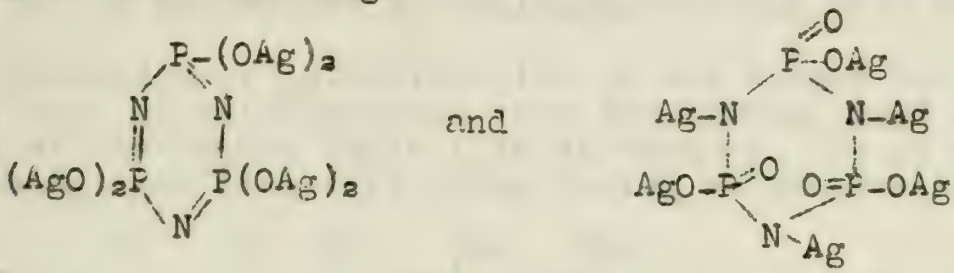
(III)

By analogy to many organic compounds, it is not unlikely that this acid could undergo transformation into the tautomeric form:

(IV)

trimetaphosphimic acid

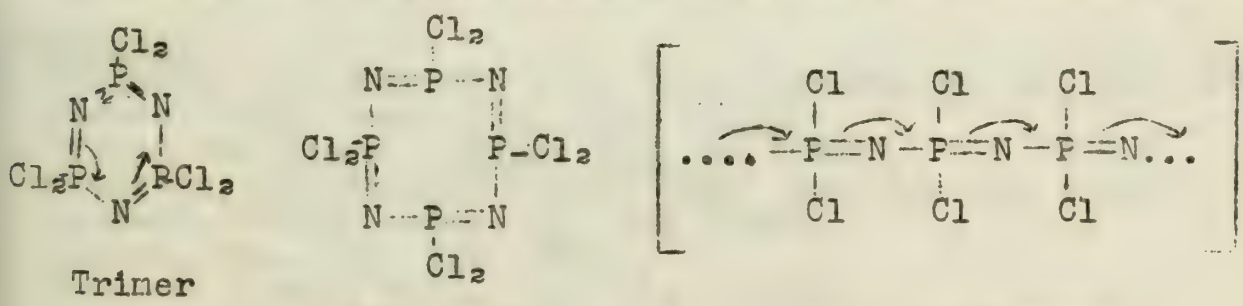
Stokes found that by properly controlling the conditions of reacting sodium trimetaphosphimate with silver nitrate, two crystalline salts could be obtained in fairly pure form. The two compounds correspond to the following:



(V)

The angle of least strain of the polygons is known to be 135°, which is most closely realized in the tetramer compound, which is the most stable of the series. Both the trimer and tetramer have been subjected to X-ray studies. The data obtained lead to the conclusion that the tetramer is in the form of a puckered ring.

Resonance occurs between the two possible arrangements of the double bonds in the rings analogous to that in aromatic compounds.



Trimer Tetramer higher polymers

(VI)

Audrieth and co-workers (1) state that "all the experimental evidence points to the fact that both the trimer and the tetramer possess cyclic structures with alternate phosphorus and nitrogen atoms, whereas the higher members including the 'inorganic rubber' possess chain structures".

An examination of the physical properties of these polymers reveals a distinct change in going from the tetramer to the pentamer. The trimer and tetramer are also less easily polymerized than the higher members which indicates their ring structures.

In addition to the definite compounds of $(PNCl_2)_x$ which have been discussed, the following have been reported: (8, 2, 3)

a. a high molecular weight oil, in which x = 11.
b. gums
c. waxes
d. inorganic rubber, with an extimated molecular weight of 20,000.
e. an infusible, non-elastic material.

Below 250°C. the trimer and tetramer give little or no polymeric material, whereas the oily polyhomologs are converted rapidly to rubbery masses below 200°C. Schenck and Römer (10) describe the polymer as an elastic and pliable material like rubber. In the pure state it is colorless and insoluble in the usual organic solvents. The elastomer is stable towards acids and alkalies but is decomposed by prolonged boiling with water.

The mechanism of polymerization of the trimer and of the tetramer, both of which possess ring structures, must be different from that of the higher chain-like structures. It is supposed that the following reactions take place during polymerization:

$$(PNCl_2)_3 \longrightarrow \ldots \overset{Cl_2}{\overset{|}{P}}-N=\overset{Cl_2}{\overset{|}{P}}-N=\overset{Cl_2}{\overset{|}{P}}-N \ldots \longrightarrow (PNCl_2)_2 + PNCl_2$$

ring rupture

or
$3PNCl_2$

In substantiation of this postulated mechanism, Audrieth and co-workers consider the depolymerization of inorganic rubber, which always gives appreciable quantities of the trimer and tetramer as well as oily and waxlike polyhomologs.

References

1. Audrieth, Steinman and Toy, Chem. Reviews 32, 99, 109 (1943).
2. Besson, Comp. rend., 114, 1264 (1892).
3. Besson and Rosset, ibid., 143, 37 (1906).
4. Gladstone and Holmes, Trans. Chem. Soc. 17, 225 (1864).
5. Laurent, Compt. rend., 31, 356 (1850).
6. Liebig, Ann., 11, 139 (1834).
7. Poulenc, Compt. rend., 75, 113 (1891).
8. Renaud, Ann., 3, 443 (1935).
9. Schenck, Ber., 60B, 160 (1927).
10. Schenck and Romer, ibid., 57B, 1343 (1924).
11. Stokes, Am. Chem. J., 17, 275 (1895); 18, 629 (1896); 19, 782 (1897)
12. Wichelhaus, Ber. 3, 163 (1870).

THE HALIDES OF SILICON

Margaret Kramer April 24, 1945

I. Introduction

The hydrogen atoms in the silicon hydrides may be replaced atom for atom by halogen. As with carbon, chain halogen derivatives may thus be built. Of the elements in Group IV, germanium alone exhibits a similarity to silicon in the formation of certain compounds.

II. Fluorine derivatives.

Only two fluorides of silicon are known, SiF_4, and Si_2F_6.

A. Completely halogenated.

1. Silicon tetrafluoride is prepared from silica or silicon and HF, or from silicon and fluorine.
2. Si_2F_6 is prepared by action of ZnF_2 on Si_2Cl_6 (1).

B. Properties.

Both of the fluorides are colorless gases, readily hydrolyzed by water.

$3SiF_4 + 3H_2O \longrightarrow H_2SiO_3 + 2H_2SiF_6$

$2Si_2F_6 + 4H_2O \longrightarrow H_2 + H_2Si_2O_4 + 2H_2SiF_6$

C. Subfluorides have been reported, but have not been established (2).

Halohydrides

A. Preparation

Recently the series SiH_3F, SiH_2F_2, and $SiHF_3$ have been prepared by action of SbF_3 on the corresponding chloride, and subjecting the products to fractional distillation (3).

B. Properties

All undergo slow disproportionation to produce SiF_4 and SiH_4.

$4SiHF_3 \longrightarrow 3SiF_4 + 2H_2 + Si$ (5)

$4SiHF_3 \longrightarrow SiH_4 + 3SiF_4$ (4)

$SiHF_3$ forms an explosive mixture with air.

III. Chlorine derivatives.

This series is more completely known, derivatives from $SiCl_4$ to $Si_{10}Cl_{22}$ having been prepared. Some of the intermediate members are not known, however.

Completely halogenated.

A. Preparation

1. $SiCl_4$ from Cl_2, SiO_2 and C at elevated temperatures; or from ferrosilicon and chlorine. Holding the temperature around 550° results in a 94% yield (6). At lower temperatures some Si_2Cl_6 is produced (7).
2. Higher members are produced from a Ca-Si alloy and chlorine if the temperature is held sufficiently low. A mixture of the following composition is thus produced:

65% $SiCl_4$
30% Si_2Cl_6
4% Si_3Cl_8
1% (Si_4Cl_{10}, Si_5Cl_{12}, Si_6Cl_{14}) separated by fractional distillation (8).

Metallic chlorides have been used as chlorinating agents; e.g., $CuCl_2$, $PbCl_2$ (2). Schwarz and coworkers have prepared $Si_{10}Cl_{22}$ by action of $SiCl_4$ and its decomposition products with hydrogen at high temperatures (9,10,11). The following mechanism was suggested to account for the formation:

$$SiCl_4 \xrightarrow{Cl} SiCl_3 \xrightarrow{SiCl_3} Si_2Cl_6 \xrightarrow{Cl} Si_2Cl_5 \xrightarrow{SiCl_3} Si_3Cl_8,$$

etc.... $Si_{10}Cl_{22}$. $SiCl_4$, Si_2Cl_6, Si_3Cl_8, $Si_{10}Cl_{22}$ were identified in the reaction products.

B. Properties

Lower members are colorless liquids. Si_6Cl_{14} and up are white solids. They hydrolyze readily, and fume in moist air. Vapors of the higher chlorides flame in air.

Increasing the temperature during the preparation of the chlorosilicons generally leads to increasing amounts of silicon tetrachloride. This fact has led to the suggestion that upon chlorination, complex silicons are first built up containing the Si-Si links originally in the element. Further chlorination plus heat cause these linkages to be broken, the final product being $SiCl_4$ (7).

An alternate view is that silicon tetrachloride is first formed which by reaction with Si produces Si_2Cl_6 etc. One objection to this is that ferrosilicon when heated with silicon tetrachloride, does not produce higher derivatives (5).

Hydrolysis of the chlorides may proceed stepwise:

$$SiCl_4 \xrightarrow{H_2O} SiCl_3(OH) \xrightarrow{H_2O} SiCl_2(OH)_2 \xrightarrow{H_2O} SiCl(OH)_3$$

$$\xrightarrow{H_2O} Si(OH)_4$$

This may be controlled by diluting the compound with anhydrous ether and using a moist organic solvent for the hydrolysis (2).

$SiCl_4$ also reacts with $(Me_4N)_2SO_3$ in liquid sulfur dioxide, precipitating $SiO_{2x}SO_2$ (12). This dissolves in excess reagent at low temperatures, but reprecipitates upon warming to 0°.

With ammonia, under temperature control, silicon tetrachloride forms a series of compounds, including $Si(NH_2)_4$, $HNSi(NH_2)_2$ ... Si_3N_4 (13).

C. Subchlorides

$(SiCl_2)_x$ has been prepared by passing $SiCl_4$ and H_2 over a glow discharge (14). $(SiCl)x$ has been prepared by cracking $Si_{10}Cl_{20}H_2$ or $Si_{10}Cl_{22}$ at 300° (10).

Halohydrides

A. Preparation

These are prepared by action of HCl on SiH_4 in the presence of $AlCl_3$. Direct reaction with halogen is explosive and must be carried on at low temperatures. $CHCl_3$ may also be used to produce higher chlorosilanes.

B. Properties -- these too hydrolyze readily and react with ammonia (15).

IV. Bromine derivatives.

The bromine derivatives both in preparation and properties resemble the chloro compounds. This series is not as completely known, however, having been prepared only as far as Si_4Br_{10}. $SiBr_4$ is a liquid, the succeeding members are crystalline solids.

Silicobromoform is spontaneously inflammable when poured through air. It hydrolyzes readily and rapidly.

V. Iodine derivatives

These are less stable than the chloro or bromo derivatives.

A. Preparation

1. SiI_4 from silicon and iodine in an atmosphere of carbon dioxide.
2. Si_2I_6 from: $SiI_4 + 2Ag \xrightarrow{300^\circ} Si_2I_6 + 2AgI$

Heating decomposes this into SiI_4 and $(SiI)_4$ (16).

Iodosilanes have been prepared from SiH_4 and HI (17). The iodosilanes are liquids with pungent odors, decomposing in sunlight. $SiHI_3$ forms an explosive mixture with air. The iodosilanes also hydrolyze readily.

VI. Mixed halides

Mixed halides containing 2 different halogens and 3 different halogens are known (18,19,20,21). Halides of the type SiWXYZ or SiHXYZ are not yet known.

The general methods for their preparation are:

$$SiCl_4 \xrightarrow[SbF_5]{SbF_3} SiF_2Cl_2 . SiF_3Cl$$

These are gases, hydrolyzable to hydrated silica, fluosilicic acid, and HCl. They have nauseating odors and are irritating to inhale (18).

$$Si_2F_6 + X_6Br_2 \longrightarrow SiF_2Br_2 + SiF_3Br + SiF_4$$

These two are colorless gases, readily hydrolyzed by moist air (19).

Complete series of chlorobromides, chloroiodides, and bromoiodides are known.

More recently derivatives containing 3 halogens have been prepared (20).

$$4SiFBr_3 + 3Cl_2 \longrightarrow 2SiFClBr_2 + 2SiFCl_2Br + 3Br_2$$

$$SiFBr_3 \xrightarrow{SbCl} SiFCl_2Br + SiFClBr_2$$

$SiFCl_2Br$ and $SiFClBr_2$ hydrolyze with ice cold water to silicic, hydrochloric, hydrobromic, and fluosilicic acids.

VII. Oxyhalides

Oxyhalides of fluorine, chlorine, and bromine are known (2,22,23).

A. Preparation

A fluoro derivative is prepared by action of SbF_3 on Si_2OCl_6.

The chloro and bromo oxyhalides are prearred by action of bromine or chlorine and oxygen on silicon at high temperatures:

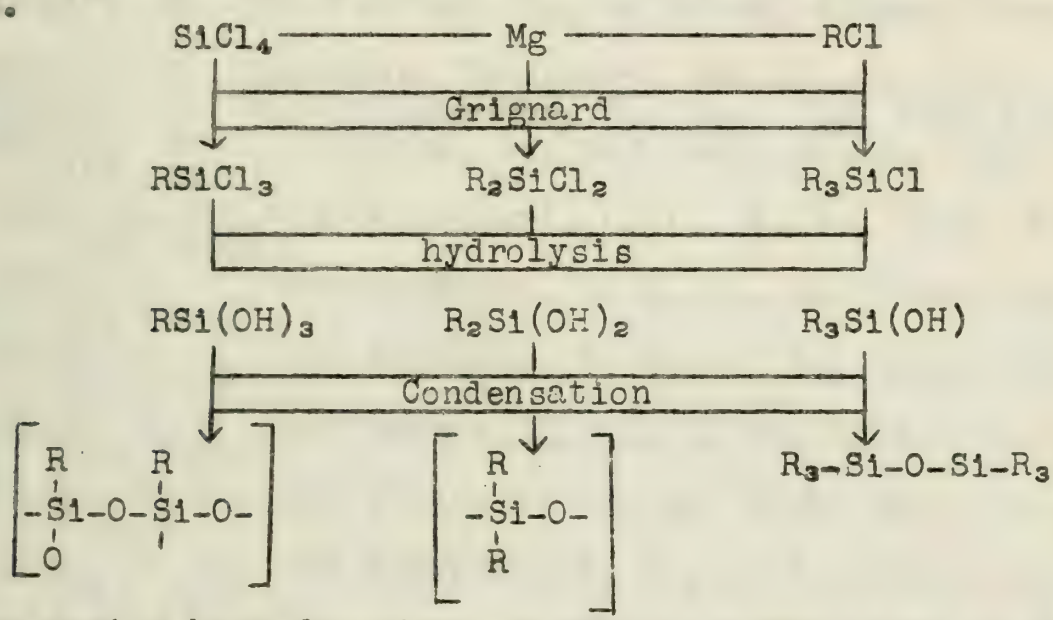
$$Si + O_2 + Br_2 \xrightarrow{700^\circ} (SiOBr_2)_4 + Si_2OBr_6 + Si_3O_2Br_8 + Si_4O_3Br_{10} + Si_5O_4Br_{12}$$

B. Properties

The oxyhalides are colorless, oily liquids, except for $(SiOCl_2)_4$ and $(SiOBr_2)_4$, which are solids. They hydrolyze readily. They react with absolute alcohol to form ethyl esters. The esters are colorless, oily liquids with high boiling points, which hydrolyze slowly, even at 100°.

II. Silicon plastics.

Recently the silicones have been shown to be of commercial importance. Since their preparation depends upon the properties of the silicon halides mentioned above, they are included briefly here.



(24, 25)

The resins have for their backbones a framework of Si atoms joined by O to each other -Si-O-Si-. The resins are much more stable thermally than the best of organic resins (26). They show relatively little change of viscosity over quite a temperature range.

The resins actually stem from the work of Kipping in England (27) who in 1937 had said that the outlook for this branch of silicon chemistry was not very hopeful.

References:

1. Schumb, W. C., and Gamble, E. L., J. Am. Chem. Soc., 54, 583, (1932).
2. Schumb, W. C., Chem. Rev. 31, 587, (1942).
3. Emeleus, H. J., and Maddock, A. G., J. Chem. Soc., 293 (1944).
4. Booth, H. S., and Stillwell, W. C., J. Am. Chem. Soc., 56, 1529 (1934).
5. Friend, J. N., Textbook of Inorganic Chemistry, V. 5, p. 187.
6. Andrianov, K. A., Compt. Rend. Acad. Sci, U.R.S.S., 28, 66, (1940) from C. A. 35, 2431.
7. Martin, G., J. Chem. Soc., 105, 2836 (1914).
8. Schumb, W. C., and Gamble, E. L. Inorganic Syntheses, V. I, p. 42.

9. Schwarz, R., and Meckbach, H., Z. anorg. allgem. Chem., 232, 241, (1937).
10. Schwarz, R., and Gregor, U., Z. anorg, allgem. Chem. 241, 395 (1939).
11. Schwarz, R., and Thiel, R., Z. anorg. allgem. Chem. 235, 252 (1938).
12. Jander, G., and Hecht, H., Z. anorg. allgem. Chem. 250, 287 (1943).
13. Emeleus, H. J., and Anderson, J. S., Modern Aspects of Inorganic Chemistry, p. 479.
14. Schwarz, R., and Pietsch, G., Z. anorg, allgem. Chem. 232, 249 (1937).
15. Ephraim, F., Inorganic Chemistry, 4th Ed., p. 637.
16. Schwarz, R., and Pflugmacher, A., Ber. 75B, 1062 (1942).
17. Emeleus, H. J., Maddock, A., and Reid, C., J. Chem. Soc., 353 (1941).
18. Booth, H. S., and Swinehcart, C. F., J. Am. Chem. Soc., 54, 4750 (1932).
19. Schumb, W. C., and Anderson, H. A., J. Am. Chem. Soc., 58, 994 (1936).
20. Schumb, W. C., and Anderson, H. A., J. Am. Chem. Soc., 59, 651 (1937).
21. Schumb, W. C., and Gamble, E. L., J. Am. Chem. Soc. 54, 3943 (1932).
22. Schumb, W. C., and Klein, C., J. Am. Chem. Soc., 59, 261 (1937).
23. Schumb, W. C., and Holloway, D. F., J. Am. Chem. Soc. 63, 2753 (1941).
24. Bass, S. L., Hyde, J. F., Britton, E. C., and McGregor, R. R., Modern Plastics, 124-128, 212-214 (November, 1944).
25. Hyde, J. F., and Delong, R. C., J. Am. Chem. Soc., 63, 1194 (1941).
26. Moses, G. L., Westinghouse Engineer 4, 138, (1944) from C. A. 38, 6006.
27. Kipping, F. S., Proc. Royal Acad. (London) 159, 139 (1937).

ROLL CALL

April 17, 1945

Synthetic Optical Crystals

A. L. Oppegard

Synthetic optical crystals of sodium chloride, potassium bromide, lithium fluoride and sodium nitrate are being made by the Harshaw Chemical Company. The crystals are 8" in diameter, 10 1/2" high, and weigh about 35 pounds. A 60° lithium fluoride prism with a 19mm. face and 15mm. high costs $1000.

The crystals are made of pure salts in platinum crucibles. The crucibles have a cone shaped bottom, weigh 850 grams and cost $900. One crucible can be used to make twenty sodium chloride crystals but can be used to make only four lithium fluoride crystals.

The platinum crucible containing the molten salt is placed in a special oven. The oven is a vertical cylinder divided into a lower and upper oven. The crucible is placed in the upper oven and is gradually lowered by a snychronous motor to the lower oven. It takes about a year to determine the optimum conditions with respect to temperature gradient and rate of lowering.

When the temperatures in the ovens are right, the lowering mechanism is started, and a cold pin placed against the tip of the cone shaped bottom to start crystallization. It is thought that the cold pin starts many microscopic crystals, and then one forges ahead to form the main crystal. The growth of the crystal takes 7-10 days, and there is no way of telling beforehand whether one crystal or several have formed.

The crystal is removed from the crucible much as an ice cube is removed from an ice tray, i.e., intense heat is applied to the outside of the inverted crucible. After annealing for 7-10 days, the crystal is ready to be split or sawed into the desired shape.

The value of these crystals lies in the fact that they are much larger than natural crystals and permit the manufacture of large prisms and other optical equipment for infra red spectographs. By the use of the infra red analysis petroleum fractions can be identified in five minutes where it used to take days by other means.

Reference

Taylor and Kremers, Chem. Ind., LV, No. 7, page 906 (1944).

Kolo Dati

April 17, 1910

Beginning Optical Corrals

A. C. Gossard

Kolo-Kolo optical corrals is a million dollar, publicity stunt, fitting finally not quite alone where the Kolo Kolo of the Burdow Chemical Company. The corrals are 48 in length, 12 in high, and weigh about 40 pounds. A 40-watt lighting system with a lamp, free and lamp, light beam source.

The corrals are made of very small is glass-ware material. The lighting lamp a some moving source, which the amount most good. The amount can be used to make twelve small colorful crystals but also be used to make only four lifelike crystals.

The platinum crucible containing the molten melt is placed in a special oven. The oven is a vertical cylinder having a lower and upper oven. The crucible is placed in the upper oven and is gradually lowered by a mechanism motor to the lower oven. It takes about a week for cooling the molten mass with regard to temperature gradient and rate of lowering.

When the temperature in the lower oven reaches, the lowering mechanism is started, and a rod, pin-shaped mounted the tip of the rare element before to start crystallization. It is usually that the melt has stable enough crystals. It is usually fingers shaped in form and in crystal. The growth of the crystal takes 7-12 days, and there is no way of telling beforehand if the crystal are crystal or several into twins.

The crystal is removed from the cooling oven as an ingot and is removed from an ingot tong, 1-4. Although part is original to the origin of the lowered material. After annealing for 7-10 days, the product is ready to be sold or mount into the finished shape.

The value of these crystals lies in the fact that they are larger than natural crystals and permit the manufacture of large prisms and other optical elements for the manufacture of instruments. By the use of the lens and mounting prisms the instruments can be identified in flame-photometry which is used to take data by other means.

Bibliography

Popular and Scientific Photo Lab., 10 No. 9, May and June 1948.

ROLL CALL

Solvent Effect of Lithium Nitrate on Zinc Acetate in Acetic Acid

Nancy Downs

Zinc acetate is only slightly soluble in acetic acid. Upon the addition of sodium or ammonium acetate the solubility of zinc acetate increases. Special chemical effects may enter into the solvent action of acetates. The authors believe that the salt effects may be large for acetic acid because of the low dielectric constant of acetic acid.

The effect of a neutral salt, lithium nitrate, on the solubility of zinc acetate was studied.

Several methods of procedure were applied. One involved the freezing points of solutions containing fixed amounts of lithium nitrate and variable amounts of zinc acetate. The solubility was obtained over the range from 40°-80°. The other method was to prepare solutions of known proportions of lithium nitrate and acetic acid, and to add excess zinc acetate. After sealing these mixtures in tubes and keeping the tubes at constant temperature for several weeks, the samples were removed and analyzed.

The results showed that lithium nitrate increases the solubility of zinc acetate but not to the same extent as the sodium acetate or ammonium acetate.

The large difference in the solubility of the zinc acetate in acetic acid containing lithium nitrate and containing sodium acetate is explained by chemical interaction in the behavior of zinc acetate to other acetates.

Reference: Griswold, Ash, and McReyholds, J. Am. Chem. Soc. 67, 3, 372 (1945).

Comparison of the Ammines of Cobalt and Copper

J. V. Quagliano

The bonding power of the $Cu-NH_3$ bond in $Cu(NH_3)_4^{++}$ is much weaker than the $Co-NH_3$ bond in $Co(NH_3)_6^{+++}$. In aqueous solution the cobalt complex is more stable, that is, much ammonia is liberated when the hexammine cupric salt is dissolved in water. As regards the bonding power and the stability of the ions, consider the electronic configurations:

	3d					4s	4p		
Cu^{++}	xx	xx	xx	xx	x				
$Cu(NH_3)_4^{++}$	xx	xx	xx	xx	..|	..|	..	..	x

The one unpaired electron in the 3d orbital "jumps" to the 4p level (these orbitals have about the same energy). The stability depends mainly on s- and p- orbitals and the configuration of the complex ion is planar.

In the case of cobalt, we have:

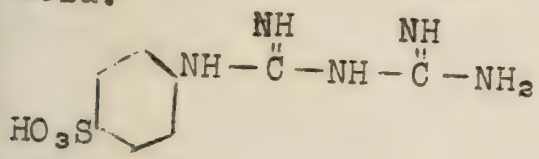
	3d			4s	4p
Co^{+++}	xx	xx	xx		
$Co(NH_3)_6^{+++}$	xx	xx	xx	.. .. | .. |	.. .. ..

In the hexammine cobaltic ion, two d orbitals are available for combination along with s and p and these six orbitals have their bonds directed toward the corners of a regular octahedron. The cobalt complexes, as is general of the complexes of the transition elements, differ from those of copper. The size and charge of the cations are not sufficient to explain the chemistry of an element, for one must also consider the covalent energy involved.

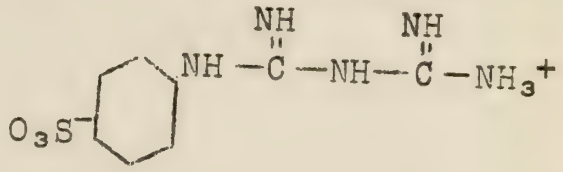
Complex Compounds of Phenylbiguanide-p-Sulfonic Acid

Margaret Kramer

Continuing a series of investigations on complexes formed by biguanide and its substitution products with Ni^{++}, Cu^{++}, Co^{+++}, Pd^{++}, and Cr^{+++}, Ray has recently reported the preparation of complexes of Co^{+++}, Ni^{++} and Cu^{++} with phenylbiguanide-p-sulfonic acid:

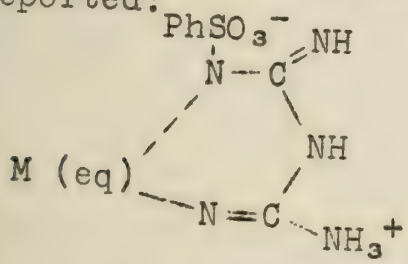


I



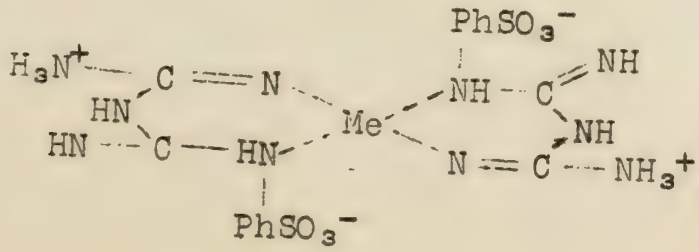
II "Zwitter ion"

The substance is practically insoluble in water due to internal salt formation. Insoluble complexes of the following type are reported:



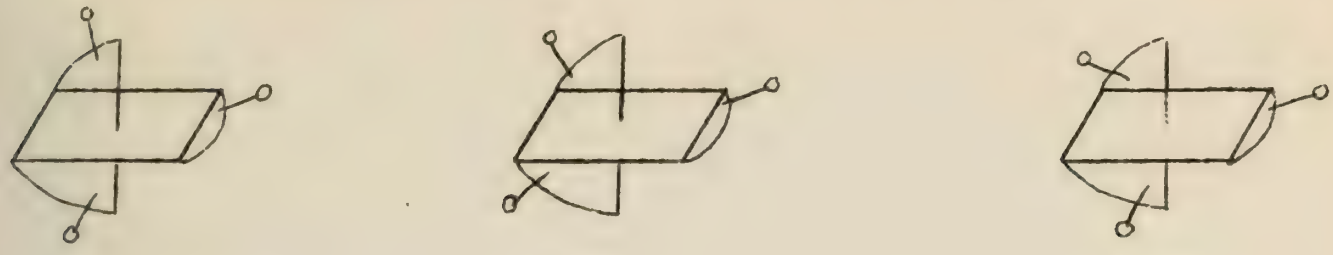
M (eq) = 1/2 Cu^{++}, 1/2 Ni^{++} or 1/3 Co^{+++}

The four-coordinated complexes of copper and nickel are planar, and show cis- trans isomerism. Only 1 form was isolated, probably the trans form, since the cis form should be relatively unsoluble because of the proximity of two negative groups:



trans

The cobalt complex (octahedral) ought to show geometric isomerism:



I II III

$\overset{\circ}{|}$ = $PhSO_3^-$

III should be most stable because of the distance of the $PhSO_3^-$ groups from each other.

Coordination with copper or nickel increases the acid character of the ampholyte. Coordination with cobalt somewhat enhances the strength of cationic acid and anionic base.

Reference:

Ray, P. and Siddhanta, S., J. Ind. Chem. Soc. 20, 250 (1943).

THE DETERMINATION OF CRYSTAL STRUCTURE

K. J. Pipenberg May 1, 1945

I. Introduction. The crystalline state has long intrigued investigators. The methods and tools of research were limited to optical methods in the visible range--which permitted a study of the outer form only. With the discovery by Friedrick, Knipping, and Laue (1) that x-rays could be diffracted by crystals which acted as three-dimensional gratings, a new door was opened--that of complete analysis of the crystalline state.

II. Methods Used. Many techniques of recording x-ray diffraction patterns have been devised; of these, four have found wide use (2-8).

A. Powder Method (2-7). An essentially monochromatic beam is permitted to impinge on a finely powdered sample. The crystal fragments of the sample are randomly orientated so that smooth concentric rings or arcs are recorded on the cylindrical film. The pattern recorded on the film is a "fingerprint" of the compound.

B. Laue Method (2-7). A single fixed crystal is placed in the path of an x-ray beam containing all wave lengths. A pattern of symmetrical spots is recorded on a flat film. Each plane in the fixed crystal selects a wave length from the x-ray beam so that the Bragg Law, $n\lambda = 2d\sin\theta$, is satisfied.

C. Rotation or Oscillation Method (2-8). A single crystal is rotated or oscillated about one of its axes in a monochromatic x-ray beam. The pattern, which consists of a series of spots lying on parallel lines, is registered on a cylindrical film, each set of planes recording only when it is in such a position that the Bragg law is obeyed.

D. Weissenberg Methods (2-8). This is a modification of the rotation technique. A single crystal is rotated about one of the principal axes while at the same time the cylindrical film is translated parallel to the axis of rotation. A shield is used so that only one layer line can be recorded at one time. The pattern obtained is a beautiful network of symmetrical spots.

II. General Procedure (4, 5, 6). There is no completely standardized procedure for the determination of a structure. Each new structure becomes a novel problem presenting fresh and unexpected difficulties. The following steps are usually encountered in one form or another.

A. A study of the external symmetry of the crystal--including such physical properties as optical, electrical, magnetic, etc.

B. The determination of the size of the unit cell.
   1. Rotation or oscillation patterns about the principal axes.
   2. Indexed powder patterns.
   3. Laue patterns -- a rough approximation.

C. The determination of the space lattice or scheme of repetition.

D. The calculation of the number of molecules per unit cell.

$$n = \frac{D\ V\ 6.03 \times 10}{M}$$

n = number of molecules per unit cell.
D = density.
V = volume in cubic angstroms.
M = molecular weight.

E. The selection of the space group.

F. The tabulation of all possible atomic arrangements.

G. The choice of the correct arrangement.

H. The determination of the parameters of this arrangement that fix the exact position of the atoms in the unit cell.
   1. Deduction method--applicable only to the simplest structures.
   2. Fourier series method.

$$\rho(uvw) = \frac{1}{V} \sum_{h=\infty}^{+\infty} \sum_{k=\infty}^{+\infty} \sum_{l=\infty}^{+\infty} F(hkl) \cos 2\pi(hu + kv + lw)$$

   3. Pattern-Harker Series.

$$P(uvw) = \sum_{h=\infty}^{+\infty} \sum_{k=\infty}^{+\infty} \sum_{l=\infty}^{+\infty} |F(hkl)|^2 \cos 2\pi(hu + kv + lw)$$

   4. Bragg's optical synthesis of Fourier Series.
   5. Huggins' modification of the Bragg method.

IV. An Example. The crystal structure of copper sulfate pentahydrate as determined by Beevers and Lipson (9) illustrates the problems encountered and the methods employed for their solution.

A. Available data which was useful.
   1. Decomposition on heating proceeds in three stages.
      $CuSO_4.5H_2O \rightarrow CuSO_4.3H_2O \rightarrow CuSO_4.H_2O \rightarrow CuSO_4$
   2. Four waters are replacable by ammonias, while the fifth is not.
   3. Jordahl (10) predicted from magnetic susceptibilities the tetrahedral arrangement of oxygens around the copper atoms.
   4. Optical examination (11) indicated a tricilinic system, with centro symmetry.
      a. Space Group -- C_i^1
      b. Axial ratio: a:b:c = 0.5715:1:0.5575.
      c. Angles: $\alpha = 82°16'$, $\beta = 107°.26'$, $\gamma = 102°40'$.
      d. Well developed [001] zone.

B. X-ray Data.

1. From oxcillation patterns the unit cell dimensions were found to be

$$a_o = 6.12 \text{ Å}$$
$$b_o = 10.7 \text{ Å}$$
$$c_o = 5.97 \text{ Å}$$

The volume of the crystal was calculated to be 363 $Å^3$.

2. The number of $CuSO_4.5H_2O$ per unit cell calculated to be 2.
3. From the extinctions noted on the photographs, the space group was found to be C_i^1 -$P\bar{1}$.
4. Determination of copper and sulfur positions.
5. The complications which arose in the establishment of the other atomic positions prevented the direct solution of the structure. The intensities of 89 (hk0) reflections were measured (12) and the Fourier projection (13) of the unit cell on the (001) plane was made, establishing the remaining positions.
6. The structure obtained was verified by a comparison of the observed and calculated (14) intensities.

C. Discussion of the structure. The copper atoms lie on the special positions (000) and $(\frac{1}{2}\frac{1}{2}0)$ and the sulfur upon the general position (0.01 0.29 0.54). Four waters are arranged in squares around the coppers, and two oxygens with these form an approximate octahedron. The fifth water is not coordinated, but is in contact with two oxygens and two waters.

Bibliography.

1. Friedrick, Knipping, and Laue, Sitzungsber. Bayr. Akad., 1912 305.
2. Clark, G. L., "Applied X-Rays", Third Edition, McGraw-Hill, New York (1940).
3. Bragg, W. H., "An Introduction to Crystal Analysis", Bell, London (1928).
4. Bragg, W. L., "The Crystalline State", Vol. I., Macmillan, New York (1934).
5. Wyckoff, R. W. G., "The Structure of Crystals", Second Edition, Chemical Catalogue Co., New York (1931).
6. Barrett, C. S., "Structure of Metals", McGraw-Hill, New York (1943).
7. Davey, W. P., "A Study of Crystal Structure and Its Applications", McGraw-Hill, New York (1934).
8. Buerger, M. J., "X-Ray Crystallography", Wiley, New York (1942).
9. Beevers, C.A., and Lipson, H., Proc. Roy. Soc. A 146, 570 (1934).
10. Jordahl, Phys. Rev., 45, 87 (1934).
11. Tutton, "Crystallography and Practical Measurement", Vol. 1, p. 297, Macmillan, New York (1922).
12. Bragg and West, Z. Kristallog., 69, 120 (1928).
13. Bragg, W. L., Proc. Roy. Soc., A 123, 537 (1929).
14. James and Brindley, Z. Kristallog., 78, 470 (1931).

Additional References:

Strukturbericht, Vol. I -- VII, Edwards Brother, Ann Arbor.

Zachariasen, W. H., "Theory of X-Ray Diffraction in Crystals", Wiley, New York (1945).

Evans, R. C., "An Introduction to Crystal Chemistry", University Press, Cambridge (1939).

Stillwell, C. W., "Crystal Chemistry", McGraw-Hill, New York (1938).

Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry". Van Nostrand, New York (1943).

Ephraim, F., "Inorganic Chemistry", translated and revised by Thorne, P. C. L., and Roberts, E. R., Fourth Revised Edition, Nordeman, New York (1943).

SIR HUMPHRY DAVY

Virginia Bartow May 8, 1945

Youth and Education -- 1778-1798.

1. Born -- Penzance, Cornwall, December 17, 1778.
2. Ancestors among the 200 year old families of Cornwall.
   a. Grandfather a builder.
   b. Father a woodcarver and farmer. Died in 1794.
   c. Mother a milliner.
3. Education
   a. Mr. Bushnell -- for reading and writing.
   b. Grammar school from six to fourteen.
   c. Truro -- The Reverend Mr. Coryton one year 1793.
   d. 1794, a year unsettled, no responsibility.
   e. 1795, Elaborate scheme of self study comprising all the Liberal Arts.
   f. 1795, Apprenticed to Dr. Borlase -- surgeon and apothecary of Penzance.
      1. Influential studies -- Mathematics, Nicholson's "Dictionary of Chemistry" and Lavoisier's "Elementary Chemistry"; Locke, Berkeley, Hume. Condorcet and Kant.
      2. Friends Gregory Watt and Davies Gilbert
      3. Essays on Heat and Light.

Establishment of Reputation, 1798-1812.

1798 1. Pneumatic Institute at Clifton near Bristol under Dr. Beddoes.

1801 Royal Philosophical Institution --
- Assistant -- Lecturer in Chemistry and Experimenter.
- Professor of Chemistry
- Establishment of Popular Lectures
- Research both of his own choosing and that of his directors.

1812 Knighted.
- Marriage to Mrs. Aprecee -- incompatibility of temperament.
- Resignation from the lectureship at the Royal Institution.
- L.L.D. and lectures at Dublin.
- Published the "Elements of Chemical Philosophy".
- Retained connections with the Institute.

Last Years.

1813-1815 European Travels -- France, Switzerland, Italy, Austria.
- Faraday, the assistant.
- Corresponding Member of the French Institute.
- Napoleon Prize of the French Institute.

1818-1820 European Travels.

1820 Return to England -- Presidency of the Royal Society

1824 North Sea Voyage -- Sweden, Denmark, Holstein, Hanover.

1827 Winter in Italy due to ill health.
1828 Last continental trip for health.
Died at Geneva May 29, 1828.

V. Estimation of Character.
A poet -- imagination.
A humanitarian -- safety-lamp.
Disposition -- spoiled by success and jealous of rivals.
tactless and irritable toward critics.
unfriendly to Faraday and Davy.
A genuine scientist -- Facility to modify prevalent belief.
Foresaw change of opinion.
Convictions based only upon proof.
Davy's place in history not due to human fraility, incidents of his life or popular audiences. His significance is scientific and the summary of his work is a review of the science of his time and its progress.

V. Scientific Interests and Achievements.
1. Essays on Heat and Light -- youthful speculation.
a. Contemporary theory of combustion -- phlogiston versus oxygen. Temporary substitution of phosoxygen -- a combination of oxygen and light.
b. Heat of Combustion -- ejection of caloric, an imponderable fluid.
-- motion or vibrations of particles.
c. Heat capacity -- products of bombustion have less capacity than original substances.
2. Physiological effects of gaseous medication -- N_2O
Contingent research -- composition of HNO_3, NO, N_2O_4 and NH_3.
3. Electrochemical studies.
Consideration of the production of hydrogen and oxygen by the electrolysis of water.
Theory-Ritter, elements at electrodes had been combined with electricity.
-Davy, a conducting chain.
Unexplainable appearance of acid and alkali at electrodes.
Contemporary definitions.
Acid -- the present oxide of a non-metal.
Oxide - A substance not sufficiently oxygenated into an acid.
Salt -- combination of an acid and oxide. (Metal part of oxide and non-metal in acid might not be known).
Trials to eliminate the acid and alkali lead to the discovery of Na, K and later, at an amalgamated electrode, Ca, Ba, Sr and Mg.
Connection established between chemical and electrical affinity.

4. Alkaline nature of K, Na and NH_3.
   K and Na do not contain hydrogen nor does NH_3 contain oxygen. (Subjected to experimental proof).
5. Study of halogens.
   a. Elementary nature of chlorine established.
      Basis -- Chemical properties.
         the "proportions" with which it combines.
         (Mr. Dalton's ingenious idea).
         Dry Cl_2 and Fe in red hot tube } -- same product
         Fe and HCl } -- without water
      Contingent discoveries -- $COCl_2$ and ClO_2--euchlorine.
         HCl, HI and HCN acids have no oxygen.
      Broadens definition of combustion.
   b. Characterized F_2 -- suspected "fluate of calcium".
   c. Solved French riddle by classifying I_2.
6. Composition of the air -- mild combinations.
   Individual gases stirred by an atmospheric turbulence.
   1833, Grahams Law -- gaseous diffusion explained later by the kinetic theory.
7. Chemistry of the diamond.
   Argument for differently arranged particles in apparently elementary forms of matter.
8. Minor experiments.
   Theory of volcanoes. Attempt to get chemical effects
   H_2Te and PH_3 from magnetic effects.
   Torpedo fish.
9. Practical and humanitarian work.
   Safety lamp -- copper for ships sheathing --
   Zinc to preserve boilers.
10. Lectures: Tanning and Agricultural Chemistry.
11. Chemical Philosophy and Predictions.
   1. Appreciation of theories, analogies and hypotheses.
   2. No formulas and no equations.
   3. Elements of bodies merely points possessing weight and attractive and repulsive forces.
   4. Intimate connection between chemical and electrical phenomena.
   5. "One good experiment is of more value than the ingenuity of a brain like Newton's."
   6. Dalton's atoms became "proportions" -- the hypothetical discarded for the practical.
   7. Natural orders of resemblance, K, Na, NH_4
      (Gay-Lussac S and O_2) Cl_2, I_2 and O_2.
   8. H_2O as a formula for water -- based on volumes.
   9. Prout's Hypothesis.
   10. Liquifaction of gases by self compression from slow generation. HCl by Davy followed by Cl_2 by Faraday.
   11. All acids contain hydrogen.
12. Conclusion --Davy's greatest success in the realm of facts.
   His attempts at theory not happy.

REFERENCES

Davy, Humphry, "The Decomposition of the Fixed Alkalies", Alembic Club Reprint, No. 6. W. F. Clay, Edinburgh, 1894.

Davy, Humphry, "The Elementary Nature of Chlorine", Alembic Club Reprint, No. 9. The University of Chicago Press, Chicago, Ill., 1906.

Davy, Humphry, "Elements of Agricultural Chemistry in a Course of Lectures for the Board of Agriculture", Longman, Hurst, Rees, Orme and Brown, London, 1813.

Davy, John, "Memoirs of the Life of Sir Humphry Davy, Bart". Longman, Rees, Orme, Brown, Green and Longman, London, 1836, 2 Vols.

Gregory, Johua C., "The Scientific Achievements of Sir Humphry Davy", Oxford University Press, London, 1930.

Ramsay, Sir William, "Essays Biographical and Chemical", Archibald Constable and Co., London, 1908, 41-56.

Wilden, Sir William A., "Famous Chemists, The Men and Their Work", Routledge and Sons, London, 1930, Chapter 7.

THE HALOGENOIDS OR "PSEUDO-HALOGENS"

Nancy Downs May 22, 1945

Definition. "Any univalent chemical aggregation composed of two or more electronegative atoms, which shows in free state certain characteristics of the free halogens, and which combine with hydrogen to form an acid and with silver to form a salt insoluble in water" (1,2).

History.

Gay Lussac first isolated cyanogen $(CN)_2$ in 1815 by heating mercuric or argentous cyanide. This was the first isolation of a "radical" as defined by Liebig (3). Liebig tried to isolate thiocyanogen by passing chlorine over silver or lead thiocyanate but he was unsuccessful. Linneman also tried to prepare thiocyanogen but succeeded instead in preparing the interhalogenoid, cyanogen sulfide ($(CN)_2S$) in 1861.

Schneider and Klason also attempted to isolate free thiocyanogen, but in 1901 Goldberg stated that free thiocyanogen had not yet been prepared.

Sommer isolated azido-carbon disulfide $(SCSN_3)_2$ but he did not recognize its true nature. In 1920 thiocyanogen was obtained by Soderback (4). With Soderback's work, new interest arose in the study of "inorganic radicals" and recently many investigations of the halogenoids--their structures, properties and compounds--have been made.

The Halogenoids.

A. General properties.

1. Activity or electromotive series (from a study of electrical conductivity measurements) F^-, ONC^-, OCN^-, Cl^-, N_3^-, Br^-, CN^-, SCN^-, $SCSN_3^-$, I^-, $SeCN^-$, $TeCN^-$ (1).
2. Similarities to true halogens.
   a. Halogenoids, in general, are quite volatile.
   b. Solid substances are apparently isomorphous.
   c. In general, they show an affinity for metals, combining directly to form salts. Silver, lead and mercurous salts are insoluble in water.
   d. In general, they form hydracids with hydrogen which in water solution are highly ionized.
   e. They are capable of forming interhalogenoid compounds such as $CN \cdot SCN$, CNN_3, etc.
   f. They form polyhalogenoid complexes such as $Cs(SeCN)_3$, $K(SeCN)I_2$, etc.
   g. Free halogenoids may be prepared, in general, (1) by chemical or electro-chemical oxidation of the hydracids or their salts or (2) by decomposition of the perhalides.

B. Possible explanation of halogenoid properties.

1. Kellermann and Birckenbach use the octet theory (1,5,6).
2. The sum of the valence electrons of the atoms in the halogenoid group can be arranged in saturated shells of eight electrons and an additional shell of seven electrons, similar to that of the halogen atoms.

3. Examples: azide (8 + 7 = 15), selenocyanate (8 + 7 = 15), azidodithiocarbonate (8 + 8 + 8 + 7 = 31).
4. Other radicals also have a total of valence electrons which can be arranged in shells of eight electrons. Ex. NO_3^- (23 = 2 x 8 + 7); OH^- (7).
5. Formula.
   outer electrons + valence e^- = 8n + 2m - 1.
   m = number of hydrogen atoms.
   n = number of atoms surrounded by octets.

IV. Thiocyanogen $(SCN)_2$.

A. Preparation.

1. The preparation of thiocyanogen suggested by Inorganic Syntheses is by the oxidation of lead thiocyanate by bromine.

$$Pb(SCN)_2 + Br_2 \longrightarrow (SCN)_2 + PbBr_2 \quad (8).$$

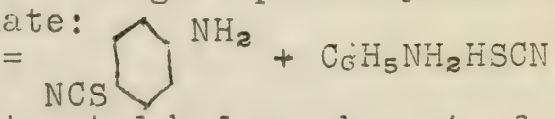
2. Solutions of thiocyanogen may be prepared by oxidation of the free acid by manganese dioxide.

$$4HSCN + MnO_2 = 2H_2O + Mn(SCN)_2 + (SCN)_2$$
$$4HCl + MnO_2 = 2H_2O + MnCl_2 + Cl_2$$

3. Thiocyanogen may also be prepared by electrolysis of thiocyanates, in alcoholic solution (16).

B. Properties

1. Physical.
   a. The solid is a crystalline material which melts at -2 to -3°C.
   b. Liquid $(SCN)_2$ can be supercooled to -20° and then at -30° it solidifies.
2. Chemical.
   a. A solution of $(SCN)_2$ in ether or carbon disulfide (1) liberates iodine from iodides (7); (2) oxidizes copper from cuprous to cupric state (3, 4); (3) combines directly with metals; (4) reacts with mercury diphenyl to yield phenyl mercuric thiocyanate; (5) reacts with aniline to give p-thiocyanoaniline and aniline thiocyanate:



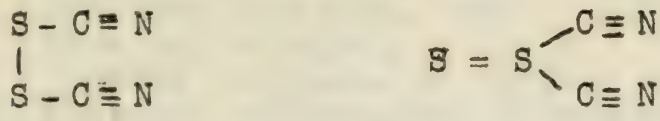
   (6) reacts with unsaturated hydrocarbons to form addition products (3): $C_2H_4 + (SCN)_2 = C_2H_4(SCN)_2$; (7) aminolysis of thiocyanogen results in formation of compounds analogous to chloramines: $(SCN)_2 + 2NHR_2 = NCSNR_2 + NHR_2 \cdot HSCN$; (8) silver thiocyanate reacts with nitrosyl chloride to form nitrosyl thiocyanate; (9) reacts directly with mercuric cyanide to form a substance of composition CN(SCN) (4).

C. Formula.

In 1922 there was doubt as to the formula of thiocyanogen but Lecher and Gaebel determined the molecular weight of thiocyanogen and found that it corresponds to $(SCN)_2$ (9). In solutions of more than one normal, there exist higher polymers.

D. Structure.

It has been proposed that thiocyanogen exists in two tautomeric forms (3).



I II

The evidence obtained by Mario Strada by his x-ray studies of thiocyanates, supports the first structure (9). He found the three atoms in a thiocyanate ion are arranged in a straight line. This is the structure suggested by Soderback.

Selenocyanogen $(SeCN)_2$.

A. Preparation.

1. Selenocyanogen has been prepared by Birckenbach and Kellerman by the electrolysis of potassium selenocyanate in alcoholic solution (1). They also prepared it by the action of iodine on silver selenocyanogen.

$2AgI + (SeCN)_2 \rightleftharpoons 2AgSeCN + I_2$

2. Kaufmann and Kögler prepared selenocyanogen (10) by the reaction of lead tetracetate in chloroform and potassium selenocyanate in dry acetone. The lead tetraselenocyanate decomposes to give selenocyanogen.

B. Properties.

1. Physical. Selenocyanogen is a homogeneous yellow powder and soon turns red in color. It is stable if dry and kept in a vacuum.

2. Chemical.

Selenocyanogen decomposes in water to form a mixture of H_2SeO_3, HCN, HSeCN.

$2Se(CN)_2 + 3HOH = H_2SeO_3 + 3HSeCN + HCN$

Selenocyanogen and carbon disulfide react when heated to form $Se_3(CN)_2$ and $Se(CN)_2$.

C. Formula.

Molecular weight determinations in benzene indicate that the formula is $(SeCN)_2$ (3). Determinations in glacial acetic acid indicate that $(SeCN)_2$ dissociates, maybe forming the unsaturated radical.

D. Structure.

1. Tautomeric forms (3).

2. Linear structure (11).

Pierre Spacu in the study of the Raman spectrum KSeCN, found that the frequency corresponds to the vibration of C≡N, and concluded that the formula of selenocyanate is N≡C-Se. Also selenocyanate is isosteric with Br-C≡N and since this is linear, one might expect selenocyanate to be linear.

VI. Oxycanogen $(OCN)_2$.

A. Preparation (1, 12).

1. Potassium cyanate reacts with a neutral (25) solution of hydrogen peroxide, cupric oxide or sodium hypobromite to form oxycyanogen.

$$2KCNO + H_2O_2 = K_2CNO_2 + CNO + H_2O$$

2. Nitrogen dioxide can be reduced by carbon at 150° to oxycanogen.
3. Cyanogen bromide reacts with silver oxide to give oxycyanogen.

B. Properties

1. Physical.

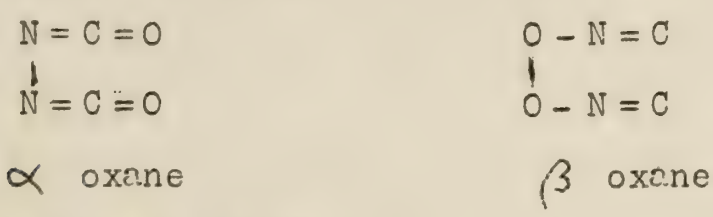
$(CNO)_2$ is a gas, lighter than carbon dioxide and may be present in human exhalation.

2. Chemical.

Oxycyanogen (a) liberates iodine from potassium iodide, (b) reacts directly with copper, zinc and iron, (c) forms interhalogenoid and halogen halogenoid compounds (13), (d) gives a white precipitate with a solution of barium hydroxide, and (e) is believed to be the anhydride of oxanic acid, H_2CNO_2.

C. Formula and structure.

Little work on the formula and structure has been done. According to Lidor, two isomeric oxanes may be obtained by varying the conditions or procedure.



α oxane β oxane

II. Azidocarbon disulfide $(SCSN_3)_2$.

A. Preparation.

1. $(SCSN_3)_2$ may be prepared by chemical oxidation of azide dithiocarbonates such as $KSCSN_3$ by H_2O_2, KIO_3, K_2CrO_4, $HgCl_2$, $FeCl_3$, $KMnO_4$, MnO_2, Cl_2, I_2 and Br_2 (14, 15). The best procedure uses the reaction of a solution of iodine in potassium iodide on a solution of potassium azidodithiocarbonate.
2. $(SCSN_3)_2$ may also be prepared by the electrolytic oxidation of a solution of $KSCSN_3$.

B. Properties.

1. Physical.

$(SCSN_3)_2$ is a white unstable crystalline solid which is slightly soluble in water. It is very sensitive to both shock and impact.

2. Chemical.(14).

a. $(SCSN_3)_2$ reacts slowly with dilute acids and rapidly with concentrated acids, liberating sulfur. Nitric acid reacts but no sulfur precipitates.

b. $(SCSN_3)_2$ reacts with alkali in a manner similar to that of chlorine at -10°C.

$$(SCSN_3)_2 + 2KOH = KSCSN_3 + KOSCSN_3.$$

On acidification:

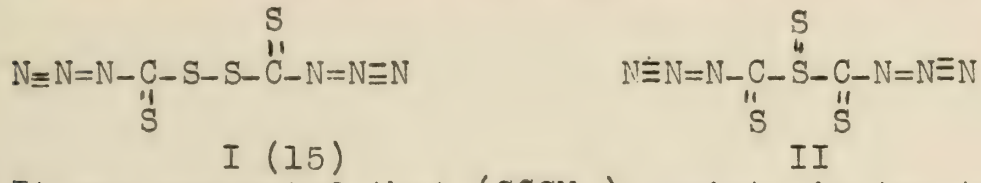
$$KSCSN_3 + KOSCSN_3 + H_2SO_4 = K_2SO_4 + (SCSN_3)_2 + H_2O$$

c. There is some indication that $KOSCN_3$ is converted to chlorate analog of azido carbon disulfide.
$3KOSCSN_3 = 2KSCSN_3 + KO_3SCSN_3$

d. $HSCSN_3$ is an acid comparable to H_2SO_4 in strength. ($K = 2.14 \times 10^{-2}$). This acid is stronger than HF, HCN and NH_3 and weaker than HCl, HBr and HI.

C. Formula and structure.

Browne and coworkers confirmed the formula $(SCSN_3)_2$.



I (15) II

It was suggested that $(SCSN_3)_2$ exists in two tautomeric forms, but Browne believes the first structure to be the correct one.

III. Cyanogen $(CN)_2$ (16).

A. Preparation.

1. $(CN)_2$ is prepared by the thermal decomposition of $Hg(CN)_2$.
2. It can be prepared also by reaction of KCN on $CuSO_4$.
3. It can also be prepared by the dissociation of AgCN.

B. Properties.

1. Physical.

Vapor density is 2.321 g/l at 19.4° and 316.6 mm. pressure. The boiling point is -21.17° and the melting point is -27.9°C. It is a colorless gas, with a distinctive odor, very poisonous and it is soluble in water.

2. Chemical.

In alkaline solution it hydrolyzes to cyanide and cyanate. It decomposes in sunlight forming ammonium oxalate, ammonium formate and urea.

C. Structure and formula.

The formula of cyanogen has been shown to be $(CN)_2$.

Cyanogen at first was believed to have a ring structure but after much spectroscopic and electron diffraction work evidence has shown that the structure is $N \equiv C - C \equiv N$. The parachor and small dipole moment seem to uphold this structure (16).

IX. Azide (N_3^-).

The preparation of the free azide has not as yet been accomplished although Browne has attempted several times to isolate it (17).

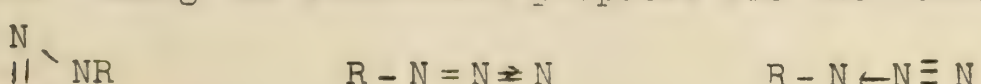
The radical has many properties similar to those of halogens.

A. Chemical properties.

1. Silver salts are insoluble.
2. Mixed halogenoids may be prepared.
3. Azides show absorption in the near ultra-violet region similar (18) to iodine.

B. Structure

Much research has been done on the structure of the azide ion. Among the structures proposed are the following:



I(19) II(20) III

The ring structure was supported by Lindemann and Thiele, who obtained parachors corresponding to ring structure, and by Hantsch who based his studies on spectroscopic absorption. The linear structures are supported by Sidgwick and Freud. Sidgwick bases his proposed structure on heats of combustion and low dipole moments (20,21).

X. Tellurocyanogen $(TeCN)_2$.

Birckenbach and Kellermann attempted to prepare $(TeCN)_2$ by the electrolysis of KTeCN in alcoholic solution but were unsuccessful (1). Little investigation has been made since those first attempts to isolate the radical.

I. Fulminate ion.

Only a few experiments on the fulminate ion have been tried thus far. Birckenbach and his coworkers have attempted to study it but with little success (3).

I. Polyhalogenoids.

Several polyhalogenoids have been prepared and their properties studied. Included are $K(SeCN)I_2$, $K(SeCN)_2I$, $K(SeCN)_3$, $Cs(SeCN)_3$ (3).

I. Interhalogen-halogenoids.

The literature lists a large number of such compounds. Included are the following:

A. Azides.

Chlorazide, ClN_3 (22,23); bromazide, BrN_3 (24); and iodoazide IN_3 (24).

B. Cyanogen compounds.

Cyanogen chloride, CNCl; cyanogen bromide, CNBr, and cyanogen iodide, CNI. (16, 25).

C. Thiocyanogen compounds: thiocyanogen chloride, SCNCl; thiocyanogen trichloride, $SCNCl_3$; thiocyanogen monbromide, SCNBr; thiocyanogen tribromide, $SCNBr_3$ (26,27).

D. Azido-carbondisulfide compounds.

$Cl \cdot SCSN_3$, $BrSCSN_3$ and Br_3SCSN_3 may exist (28).

E. Oxycyanogen compounds: iodoxycyanate, ICNO (13); bromoxycyanate OCNBr.

. Interhalogenoids.

Recent work in the halogenoid field has been devoted almost exclusively to the study of the structure of halogenoids and interhalogenoid compounds.

Among the interhalogenoid compounds studied are the following: cyanazide, CNN_3 (24), cyanogen thiocyanate (CN·SCN), cyanogen selenocyanate (10, 27); cyanogen azidodithiocarbonate $CN \cdot 3CSN_3$ (27), thiocyanogen azidodithiocarbonate $SCN \cdot SCSN_3$ (14)

Recently Birckenbach and his coworkers have tried to extend the term "halogenoid" to include many inorganic radicals including many divalent radicals.

REFERENCES:

1. Birckenbach, L., and Kellermann, K., Ber. 58B, 786-94, 2377 (1925).
2. Smith, G. B. L., Browne, A. W. and others, J.A.C.S. 56, 1116-18, (1934).
3. Audrieth, L.F. and Walden, P., Chem. Rev. 5, 339-59 (1928).
4. Soderback, E., Ann. 419, 217 (1919); C.A. 14, 1808 (1920).
5. Birckenbach, L. and Kellermann, K., Ber. 64B. 218-27 (1931).
6. Birckenbach, L. and Kellermann, K., Ber. 67B, 1729-34 (1931).
7. Kaufmann, H. P., and Kögler, F., Ber. 58, 1553 (1925).
8. Booth, H. S., "Inorganic Syntheses", p. 84, McGraw-Hill, New York (1939).
9. Strada, Mario, Gazz. chim. ital. 64, 400-9 (1934), C.A. 28, 6382 (1934).
0. Kaufmann, H. P. and Kögler, F., Ber. 59, 178 (1926).
1. Spacu, Pierre, Bull. soc. chim. [5] 3, 2074-6 (1936).
2. Lidor, A. P., C.A. 6, 2368, 2369, 3093, 3094 (1912).
3. Birckenbach, L. and Linkard, M., Ber. 62B, 2261-77 (1929); Ber. 63B, 2544-58 (1930).
4. Browne, A. W. and others, J.A.C.S. 45, 2541 (1923).
5. Sommer, F., Ber. 48, 1833 (1915).
6. Cook, R. P. and Robinson, P. L., J. Chem. Soc. 1935, 1001.
7. Browne, A. W. and Lundell, G.E.F., J. Am. Chem. Soc. 31, 435 (1909).
8. Levene, P. A. and Rothen, A., J. Chem. Phys. 5, 985-8 (1937).
9. Hantsch, A., Ber. 66B, 1349-54 (1933).
0. Sidgwick, N.V., Trans. Faraday Soc. 30, 801 (1934); J. Chem. Soc. 1929, 1108-10.
1. Frivel, L. K., J. Am. Chem. Soc. 58, 779-82 (1936).
2. Browne, A. W., Frierson, W. J., and Kronrad, J., J. Am. Chem. Soc. 65, 1696, 1698 (1943).
3. Ephraim, F., "Inorganic Chemistry", Fourth English Edition, Thorne, P.C.L., and Roberts, E.R., Nordeman, New York (1943).
4. Yost, D. M., and Russel, H. R., "Systematic Inorganic Chemistry". Prentice-Hall, New York (1944).
5. Beach, J. Y. and Turkevich, A., J. Am. Chem. Soc. 61, 299 (1939).
6. Baroni, A. Atti. accad. Lincei, Classe sci. fis. mat. nat. 23, 871-3 (1936).
7. Audrieth, L. F. and Browne, A. W., J. Am. Chem. Soc. 52, 2799 (1930).
8. Browne, A. W. and Gardner, W. H., J. Am. Chem. Soc. 49, 2759 (1927).

Inorganic Seminar

1945-46

Table of Contents

Table of Contents -2

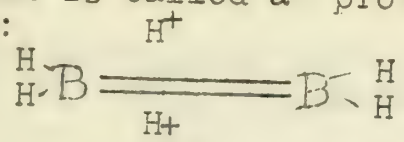
Eclectron Deficient Molecules

Principles of the Boron Hydride Structure

Hans B. Jonassen October 23, 1945

K. S. Pitzer, Journ. Am. Chem. Soc. 67, 1126 (1945)

In this theoretical paper Pitzer postulates a new structure to explain the physical properties of the boron hydrides. The structure proposed is called a "protonated double bond" and is given as follows:



This structure is similar to the boron hydride structure postulated by Longuet-Higgins and Bell,[1] Dilthey,[2] and Core.[3] The "argentated double bond" proposed for the butadiene silver complexes has a similar structure.[4]

This protonated double bond

1) is formed between electron pair bonded groups of general formula R_nMH where n+1 is less than the number of valence shell orbitals of atom M.
2) uses one hydrogen atom and one vacant orbital in each group.
3) is stable because there exists a moderate increase in electron density around the protons.

The orbital characteristics of the new bond are

1) M has two bonding orbitals at bonding angles not much greater than 100°.
2) The hydrogen atom has an s orbital available.

The most important properties of the boron hydride which can be explained by this structure are:

1) Protons increase the boron-boron distance. This is in reasonably satisfactory accord with the electron and X-ray diffraction data.
2) The bond resists twisting as a double bond. This is in agreement with the infrared and vibration spectra.
3) The double bond protons can be removed by acids; however, no experimental proof is given for this statement.
4) Presence of two protons enhances the ease of breakage of the double bond; this is in accord with the fact that the B_2H_6 molecule splits when more than 4 of the hydrogen atoms are substituted.
5) Electronic spectra are very similar to the double bond spectra, because the protons can not move appreciably in the time of electronic transition.
6) High atomic polarization of B_2H_6[5] as compared with 0.0 polarization for ethane favors the protonated double bond structure. Similar conclusions may be reached from the highly polar nature of B_2H_6 in its reaction with ammonia.[6]

7) Specific heat, optical spectra, and diamagnetic susceptibility data also favor this structure.

8) The theory is consistent with wave mechanics.

Pitzer also explains the absence of triborates by this structural theory although some of the reaction mechanisms proposed are rather out of the ordinary.

The structure postulated here is a development of the structures proposed by Wiberg[7], and Longuet-Higgins and Bell[1].

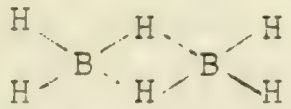
Bibliography

[1]Longuet-Higgins and Bell, Jour. Chem. Soc. 1943, 250
[2]Dilthey, Zeit. angew. Chem. 34 596, (1921)
[3]Core, Chem. and Ind. 5, 642, (1927)
[4]Winstein and Lucas, J. Am. Chem. Soc., 60 836, (1938)
[5]Ramaswamy, Proc. Indian Acad. Sci. 2A 364, 630, (1935)
[6]Eistert, Z. phys. Chem. B52 202, (1942)
[7]Wiberg Ber. 69 B, 2816 (1936)

THE STRUCTURE OF DIBORANE

Margaret Kramer October 23, 1945

Further ideas on the structure of diborane are discussed by Burowoy[1] who bases his interpretation on the structure originally proposed by Longuet-Higgins and Bell.[2]



The linkages on the hydrogen, different from other hydrogen bonds, were called resonance links by Longuet-Higgins and Bell.

Burawoy believes the hydrogens are electrostatic in nature for the following reasons:

1) The presence of opposite charges on the 2 atoms (the B is positive, the H is negative).
2) The chance for close approach of the atoms because of their small sizes. He admits that the interpretation of the infra-red spectrum will doubtless indicate the structure more specifically.

In reply to the above, Longuet-Higgins and Bell[3], while agreeing that their approach is not the only one, discount the electrostatic hydrogen bond for the following reasons:

1) If a dipole were present, polymerization would not necessarily stop with B_2H_6--higher polymers would be possible.
2) The small size of the boron atom is not a decisive factor for hydrides of Al and Ga are dimeric.
3) Calculations[4] of the normal vibrations of the B_2H_6 molecule indicate the hydrogen to be the same distance from each boron. This would not be true if the hydrogen bond were electrostatic.

---

[1] Burawoy Nature, 155, 328, 1945)
[2] Longuet-Higgins and Bell J. Chem. Soc., 250, (1943)
[3] Bell and Longuet-Higgins Nature, 155, 328, (1945)
[4] Bell Proc. Royal Soc. 183, 328, (1945)

A Mineralogist Talks to Chemists

T. T. Quirke October 30, 1945

A geologist goes back to minerals as a chemist goes back to atoms. "A mineral is an inorganic substance of definite chemical composition which occurs in nature." Since minerals occur in nature, they are stable substances, and they are therefore limited in number of varieties. Their limited number makes identification comparatively easy. The limited number of minerals which occur in igneous rocks, together with the uniformity of chemical reactions under conditions of high temperature and pressure which control their development, makes possible optical methods of petrographic analysis. These methods are very rapid by comparison with usual chemical procedures.

The stability of the commoner minerals often results in their being economically unusable as sources of metals.

Mineralogists have a "phase rule" similar to that of the chemists. The mineralogist's version is that "the number of minerals in a rock is equal to the number of constituents of which the rock is composed." The mineralogist's "constituents" are usually oxides: CaO, SiO_2, etc.

The formation of crystal generations of the same common mineral, derived from a molten source containing relatively rare elements, almost always results in replacement of a plentiful atom by atoms of a closely related rare element in the later-formed crystals. For example cesium and rubidium are found in the late orthoclase crystals, replacing potassium, and not in the first-formed crystals. Futhermore lithium and other less related rare elements also are concentrated in other minerals with the late-forming orthoclase crystals.

Chemists and geologists working together would form an advantageous combination in searching for rare minerals. Many minerals might be found to be less rare than is now supposed.

ROLL CALL

Basic Strength of Ammonia and the Methylamines

Mark M. Woyski November 6, 1945

Herbert C. Brown J. Am. Chem. Soc. 67, 378 (1945)

On the basis of the inductive effect of the methyl group the base strength (or donor ability) of the ammonia molecule should increase regularly with the number of methyl groups substituted for hydrogen. Actually the basic strength (relative to the proton as reference acid) increases up to R_2NH and drops for R_3N. This fact may be interpreted on the basis of steric hindrance. The bond angles in the ammonia molecule are 90°; the introduction of larger groups increases these angles until in R_3N the angles exceed the tetrahedral angle. In this case bond strain results when the molecule assumes, or attempts to assume, the normal tetrahedral ammonium ion structure or formation of a salt. This steric interference of the methyl groups prevents the formation of a coordinate covalence of maximum strength, or, it is said, the base strength is diminished.

The authors have termed this 'B'-strain' at the 'back' of the molecules as distinguised from the front where salt formation takes place.

The relative base strength of ammonia and the methyl amines is also dependent on the reference acid. It will be seen that steric hindrance may be introduced if the acid molecule is large or has large attached groups. (F-'Strain') It will also be obvious that steric effects will be greater the greater the number of hindering groups on the base so that, comparing the base strength of ammonia and the methyl amines against progessively more highly hindered acids the order of base strength will be found to change from the initial order (proton or hydronium ion as reference acid).

$R_2NH < RNH_2 < R_3N < NH_3$
to $R_2NH < RNH_2 < NH_3 < R_3N$
to $RNH_2 < NH_3 < R_2NH < R_3N$
to $NH_3 < RNH_2 < R_2NH < R_3N$

Data on dissociation constants of compounds of ammonia and amines with trimethyl and tributyl boron support these views.

I should like to point out that this may also be explained, in part, by adopting the view that introducing larger groups into an acid such as trimethyl soon decreases its acid strength.

ROLL CALL

Habit Modification of Ammonium Dihydrogen Phosphate Crystals[1]

J. A. Mattern November 6, 1945

When ammonium dihydrogen phosphate is crystallized from pure solution, its crystal consists of a second order prism in combination with a second order bypyramid. When crystallized from solutions containing certain metal ions, the prism faces are tapered as much as 16°.

Ions which produce taper		Ions which produce no observable taper		
Sn^{+4}	Au^{+3}	Hg^{+2}	Ni^{+2}	Tl^{+}
Cr^{+3}	Al^{+3}	Cu^{+2}	Ag^{+}	K^{+}
Fe^{+3}	Be^{+2}	Zn^{+2}	Ca^{+2}	Na^{+}
Ti^{+4}		Pb^{+2}	Ba^{+2}	

It is seen that small, highly charged, cations are the ones which produce this modification of crystal habit. These positive ions are adsorbed on the crystal lattice, expecially at points where the concentration of negative $H_2PO_4^-$ ions is the highest. A study of the crystal structure[2] shows that the concentration of $H_2PO_4^-$ is the greatest on the prism faces and second greatest in alternate layers of the pyramid faces. Adsorption, then, will be very pronounced at the intersection of prism and pyramid faces when the latter consists of $H_2PO_4^-$ ions. When the next layer of $H_2PO_4^-$ ions in deposited they will be pulled in a little closer because of attraction for the adsorbed positive ions. Thus, stepwise, the prism face is drawn in and the observed taper is produced.

With Sn^{+4} and Cr^{+3} ions of sufficiently high concentration, it was found possible to prevent crystal growth entirely.

Previous investigations of adsorption with consequent modification of crystal habit has been reviewed by W. G. France.[3]

References
[1]Kolb and Comer, J.A.C.S. 67, 894 (1945)
[2]Hendricks, Am. J. Sci., 14, 269 (1927)
[3]Alexander, "Colloid Chemistry", Reinhold Publishing Corp., New York, N. Y., 1944 Vol. 5, p. 443

ROLL CALL

The Preparation and Properties of Chlorine Azide[1]

C. G. Overberger November 6, 1945

The meager information concerning the properties of chlorine azide is undoubtedly due to the extremely explosive character of the compound which in undiluted condition detonates violently without apparent provocation.

Preparation

1) $AgN_3 + Cl_2 \longrightarrow AgCl + ClN_3$

2) Method of Raschig[2]. The gradual addition of acetic acid to equimolar amounts of sodium azide and sodium hypochlorite in aqueous solution. The reaction may be expressed by the following equilibrium

$$HN_3 + HOCl \rightleftharpoons ClN_3 + H_2O$$

Properties

1) Physical: boiling point, approximately -15°; melting point, approximately -100°; it is slightly soluble in water and readily soluble in most organic solvents.

2) Chemical

a) Probable behavior toward liquid ammonia

$$ClN_3 + 2NH_3 \longrightarrow NH_2Cl + NH_4N_3$$

If the ammonia is greatly in excess

$$3ClN_3 + 8NH_3 \longrightarrow N_2 + 3NH_4Cl + 3NH_4N_3$$

b) Behavior toward pentane

$$ClN_3 + C_5H_{12} \longrightarrow HN_3 + C_5H_{11}Cl$$

c) Behavior toward metals

$$4ClN_3 + 6\begin{matrix}Na\\Mg\\Zn\end{matrix} \longrightarrow 4NaCl + 3N_2 + 2NaN_3 \text{ (violent reaction)}$$

If a nonaqueous solvent is used the reaction is less violent.

d) Behavior toward phosphorus

When a few drops of pure liquid chlorine azide were condensed upon yellow phosphorus at -78°, a spontaneous detonation occurred in every case after the lapse of a few minutes. It may be ascribable either to the liberation of azine which would probably detonate with extreme violence or to the formation of an unstable phosphorus azide or complex chloro azide.

e) Reaction of chlorine azide with silver azide[3]

$$2ClN_3 + 2AgN_3 \xrightarrow{-78°} \underset{\text{(blue)}}{2N_3AgCl} + 3N_2$$

White still below 0°C, the azino silver chloride decomposes to give $2N_3AgCl \longrightarrow 2AgCl + 3N_2$

REFERENCES

1) Frierson, Kronrad and Browne, J. Am. Chem. Soc., 65, 1696 (1943)

2) Raschig, Ber. 41, 4194 (1908)

3) Frierson and Browne. J. Am. Chem. Soc., 65, 1698 (1943)

SOLUBILITY OF CESIUM ANTIMONY CHLORIDE IN HYDROCHLORIC ACID SOLUTIONS AT 25°C.

Henry Holtzclaw November 27, 1945

Ref: Bender, J. Am. Chem. Soc. 67, 1771 (1945).

The isolation or purification of cesium salts is usually accomplished by precipitation from a hydrochloric acid solution of the double salt cesium antimony chloride. Until the work described herein, however, no previous satisfactory data on solubilities in this system had been determined.

In the experimental work, spectroscopically pure cesium chloride and standard analytical reagents of other materials were used. Analytical determination of antimony was accomplished by titration with tenth normal iodine solution, standardized against arsenic trioxide. Hydrochloric acid solutions were standardized gravimetrically by precipitation of silver chloride. A Bausch and Lomb Littrow Quartz Spectrograph was used for spectrographic determinations.

In the determination of solubilities, temperature was maintained at 25.00± 0.05°C. Duplicate samples were taken each time, equilibrium being checked by analyzing additional duplicate samples taken after extra time had elapsed. A pycnometric method of density determination was used to convert results to the volumetric basis. The probable error in solubility data is about 0.3%.

The double salt which was used showed an antimony content of 25.38 ± 0.05%, substantiating the composition 3 CsCl . $2SbCl_3$ (calculated 25.33 ± 0.05% antimony). A difference in color of the double salt was noted for various conditions of preparation. In all cases, however, the salt showed the same composition. In cases of recovery of the salt by routine methods, thallium was found to be the cause of the darker color, 0.005% thallium in the cesium chloride being sufficient to produce darkening.

Table of solubility of cesium antimony chloride in hydrochloric acid solutions at 25°C.:

Molality of HCl	Grams salt/100 grams solvent	Grams salt/100 cc solution
2.086	1.732	1.778
2.953	1.389	1.444
4.027	1.236	1.304
4.869	1.178	1.256
6.875	1.114	1.217
9.957	1.083	1.218
12.92	1.093	1.258
16.20	1.134	1.333

Results show sufficient solubility to make practical the separation of cesium from the filtrate. The suggestion is made for use of stannic chloride to precipitate Cs_2SnCl_6.

Rearrangements in Compounds of Carbon, Silicon, Germanium, and tin containing Halogens, Isocyanate, and Thiocyanate.

R. W. Parry November 27, 1945

Forbes and Anderson - J.A.C.S. 67 1911 (1945)
Forbes and Anderson - J.A.C.S. 66 931 (1944)

Fundamental calculations by Urey and coworkers on isotopic exchange equilibria emphasize the fact that not even units so closely similar as isotopic atoms attain a truly random distribution among similar molecules; however, Calingaert and coworkers found that random exchange of organic radicals occurs, within experimental error, among certain alkyls, chloroalkyls, and esters and among different halogen atoms of ethylene halides. They were able to make quantitative equilibrium predictions based on the laws of probability only. Chemical or energy factors did not seem to influence the random distribution.

This work of Calingaert has been extended by Forbes and Anderson to a number of halides, isocyanates, and thiocyanates of Group IV A elements. The mixtures chloroform and bromoform; methylene chloride-methylene bromide and methylene chloride-methylene iodide were heated in sealed tubes in the presence of moistened $AlCl_3$ and KCl. At equilibrium, mixtures were analyzed by a form of fractional distillation. That distribution was very nearly random is shown by the data for an original mixture of $CHCl_3$ and $CHBr_3$.

Orig. Mixture		% $CHCl_3$	Equil. Mixture % $CHCl_2Br$	% $CHClBr_2$	% $CHBr_3$
3.0ml. $CHCl_3$ 2.1ml. $CHBr_3$	observed.	17	43	31	9
	calc. for random dist.	17.4	41.4	32.6	8.6

Random distribution was also observed for the methylene halides.

b) The equilibrium constant for the reaction $4SiCl_3SCN \rightleftharpoons 3SiCl_4 + Si(SCN)_4$ was determined by this same technique as K (Mole fractions) = 0.11

c) Studies of $Si(NCO)_4$ and $Si(SCN)_4$ revealed the probable existence the new compound $Si(NCO)_3SCN$ boiling at 126°C under 28 m m pressure. Isolation of the compound was considered possible, but has not yet been attempted.

d) Studies of $GeCl_4$ and $Ge(NCO)_4$ indicated the probable existence of a very unstable compound $GeCl_3NCO$ boiling at 112° and 760 mm.

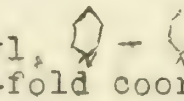
The stability of compounds produced on rearrangement decreases from carbon to tin and from chlorine to iodine [i.e. with decreasing electronegatively of the halogen or psuedohalogen].

ROLL CALL

Researches on Residual Affinity and Co-Ordination XXXVIII

James V. Quagliano November 27, 1945

Burstall, J. Chem. Soc. 1938 1672.

2 : 2' : 2" : 2''' tetrapyridyl,  , is a molecule which functions as a four-fold coordinating group. Polypyridyls are bases in which two or more pyridine rings are linked but not fused together. Six isomeric dipyridyls are known but only 2 : 2' dipyridyl has noteworthy properties as coordinating agent toward metallic salts. The linkage necessary for coordination is = N - C - C - N = . Burstall has made the di, tri, tetra, penta, and hexapyridyls. The tetramine combines with many metallic salts forming coordination compounds of the type: $[M^{+}$ tetrpy$]X$, $[M^{++}$ tetrpy$]X_2$, and $[M^{+++}$ tetrpy$]X_3$. These compounds contain only one molecule of base per ion of metal and differ from compounds containing two molecules of dipyridyl per ion of metal. Morgan and Burstall prepared salts of Fe, Co, Ni, Cu, Ag, Zn, Cd, and Pt, having anticipated that tetrapyridyl could function as a quadridentate coordinating unit.

Univalent Salts: Reactions of Ag^{+}.

$$AgNO_3 + \text{tetrpy} \xrightarrow[\text{solution}]{\text{alcohol}} [Ag^{+}\ \text{tetrpy}]NO_3 \text{(yellow)}$$

This compound resembles $[Ag^{I}$ 2 dipy$]$ NO_3 in appearance but the silver ion in the former compound is not oxidized to the divalent state by persulfate, $(S_2O_8^{=})$

Divalent Salts:

$$FeSO_4 + \text{tetrpy} \xrightarrow[\text{solution}]{H_2O\text{-alcohol}} [Fe\ \text{tetrpy}]SO_4.4H_2O \text{ reddish-brown}$$

$$\downarrow \Delta\ 120^{\circ}$$

$$[Fe\ \text{tetrpy}]SO_4 \text{ green-yellc}$$

$$CoCl_2 + \text{tetrpy} \xrightarrow[\text{solution}]{\text{alcoholic}} [CO\ \text{tetrpy}]Cl_2.\ 2H_2O \xrightarrow{H_2SO_4}$$

$[Co\ \text{tetrpy}]Cl_2.\ H_2O$ brown Pink

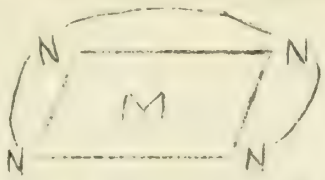
$[Ni\ \text{tetrpy}]Br_2.\ 2H_2O$, $[Cu\ \text{tetrpy}]\ Br_2\ 1/2\ H_2O$, $[Zn\ \text{tetrpy}]\ Cl_2.\ H_2O$, $[Cd\ \text{tetrpy}]\ Cl_2.H_2O$, and $[Pt\ \text{tetrpy}]\ [PtCl_4]$, were also prepared.

Trivalent Salts:

$$[Co^{III}\text{tetrpy}]\ Cl_2.2H_2O \xrightarrow[2NHCl]{H_2O_2} [Cr^{III}\ \text{tetrpy}\ Cl_2]\ Cl.\ 3H_2O \text{ grey-green}$$

$[Ir^{III}\ Cl_2\ \text{tetrpy}]_3\ IrCl_6$ was also prepared.

Morgan and Burstall regard 2 : 2' : 2" : 2''' tetapyridyl as having four pyridrine rings in one plane and state that when the four nitrogen atoms are all co-ordinated to one metallic ion, the base and the metal lie in the same plane,



With compounds of the types [M tetrpy] X and [M tetrpy] X_2, a simple planar arrangement exists. Compounds of the type [M tetrpy X_2] X have an octahedral configuration with the X groups in the trans positions; only one isomer could be obtained. Morgan and Burstall do not prove conclusively the configurations of the compounds but state only that they are most in keeping with physical and chemical properties.

Tetrpy = 2 : 2' : 2" : 2''' tetrapyridyl

dipy = 2 : 2' dipyridyl

Hydrogen Fluoride as a Solvent

Robert Burton

December 10, 1945

Solutions in hydrogen fluoride have been studied but little until the last fifteen years. This is probably due to the fact that experimental difficulties are very great in that special gold or platinum apparatus is required, and also that hydrogen fluoride is a very dangerous poinson. Scheele, Davy, Thenard, Faraday, Fremy, and Moissan all suffered from poisoning and several other early investigators were killed.

Frémy (1) was the first to prepare pure anhydrous hydrogen fluoride, and his method of preparation is still used (2). Gore (3) studied solubilities and conductivities of some few inorganic compounds in hydrogen fluoride. Little more was done until Fredenhagen and co-workers begin their investigations in 1928 (6, 7, 8, 9, 10, 11, 12).

Anhydrous hydrogen fluoride attacks the alkali metals in the same way as water does, but other metals do not react, or react only superficially.

The halogen halide is quantitatively evolved and the corresponding fluoride is formed with the halides of the alkali and alkaline earth metals and cerous chloride, manganous chloride, and ferrous chloride. The hydroxides of and oxides of most metals react more or less vigorously. Hydrogen fluoride liberates chlorine dioxide from chlorates, hydrogen cyanide from cyanides, hydrazoic acid from azides, and silicon tetrafluoride from potassium fluosilicate. It is an excellent dehydrating agent and is miscible with water in all proportions.

Table 1

Physical Properties of HF and Related Compounds

	Freezing Point °C	Boiling Point °C	Molar Heat of Fusion Calories	Molar Heat of Vaporization Calories	Dielectric Constant
HF	-83	19.5	1,090 -3	6020	83.5 (0°C)
HCl	-114	-85.8	500	3,600	4.60 (27°C)
HI	-53.6	-36	720	4,400	2.9 (22°)
H_2O	0	100	1,340	9,720	80. (20°)
H_2S	-85.5	-61.8			5.75 (10°)
NH_3	-77	-38.5	1,840		14.9 (24.5°)
PH_3	-132.5	-86.4			2.71 (-25°)
HCN	-13.8	26.5			95 (21°)

The specific conductivity of hydrogen fluoride is less than 1.4×10^{-5} (5); the dielectric constant is 174.8 at -73°, 134.2 at -42°, and 83 at 0°C. (4).

A comparison of the properties of hydrogen fluoride with those of the other substances in Table I indicates that hydrogen fluoride is a highly associated, polar substance, and it would be expected to be an excellent solvent, which it is. Its acidic nature, or non-accepting properties, make it quite different from water.

Gore made qualitative solubility measurements as did Franklin (18), but Frendenhagen and Cadenbach made the first careful determinations. Their results are summarized in Table 2.

Table 2

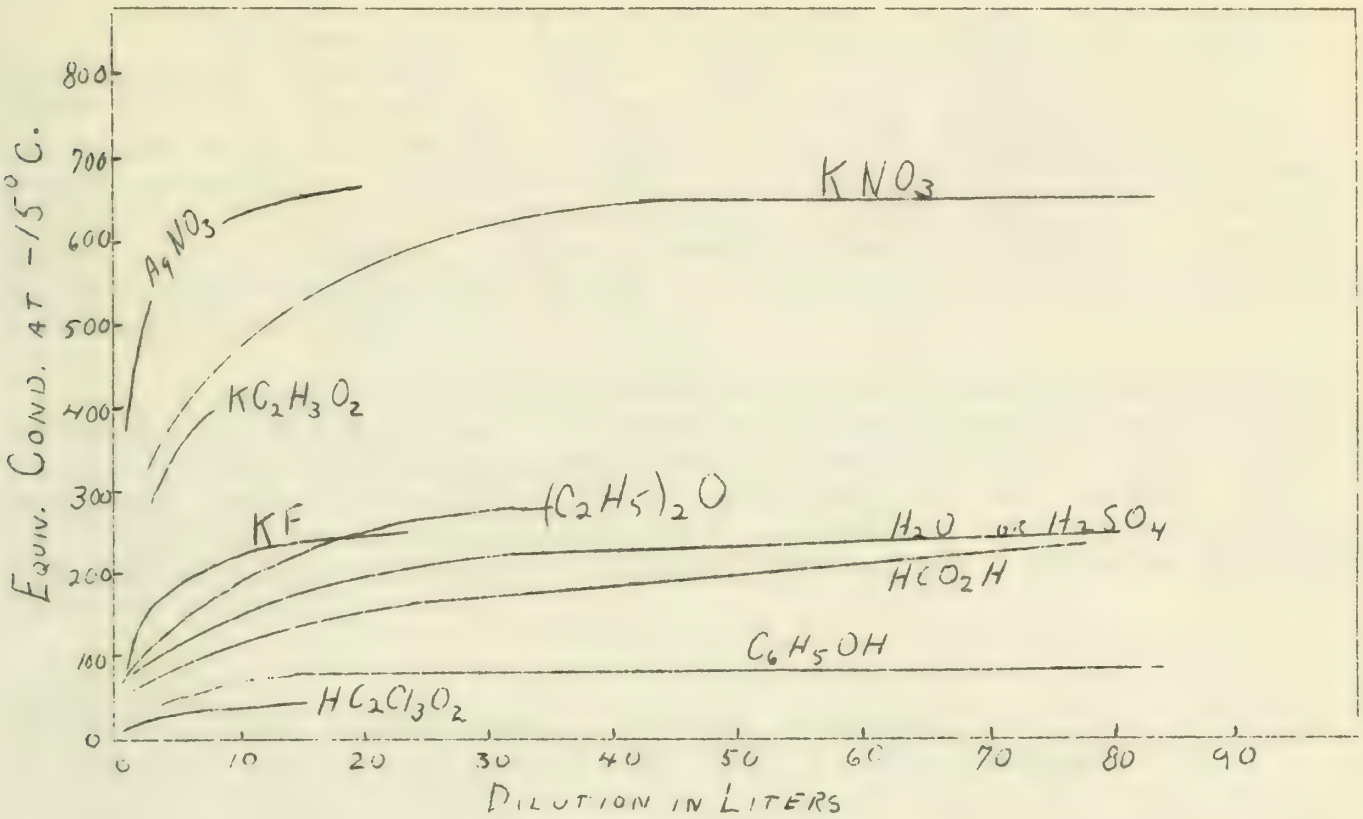
Solubility of Inorganic Substances in Hydrogen Fluoride

Soluble	Slightly Soluble	Insoluble	Soluble with reaction
H_2O	MgF_2	AlF_3	alkali halides
NH_4F	CaF_2	ZnF_2	alkaline earth halides
TiF	SrF_2	FeF_3	KCN
NaF	BaF_2	PbF_2	NaN_3
KF	$CaSO_4$	CuF_2	K_2SiF_6
RbF	$KClO_4$	HgF_2	$KClO_3$
CsF	H_2S	HCl	$BaClO_3$
TlF	CO	HI	Hydroxides
Ag^+	CO_2	HBr	
$Hg(CN)_2$		HN_3	
HNO_3		SiF_4	
$NaNO_3$		$Cu(NO_3)_2$	
$AgNO_3$		$Bi(NO_3)_3$	
K_2SO_4		$Pb(NO_3)_2$	
Na_2SO_4		$Co(NO_3)_2$	
Organic molecules		$ZnSO_4$	
Containing		$CdSO_4$	
O, S, N, or C=C		$CuSO_4$	
		Ag_2SO_4	

React. Product Insol.

React. Product Insol.	Insoluble Unreactive
$AlCl_3$	$ZnCl_2$
$FeCl_2$	$SnCl_2$
$MnCl_2$	$NiCl_2$
$CeCl_3$	$CdCl_2$
MgO	$CuCl_2$
CaO	HgI_2
SrO	AgCl
BaO	AgBr
PbO	AgI
BaO_2	HgO
Al_2O_3	PbO_2
CuO	MnO_2
	SnO_2
	Cr_2O_3
	WO_3
	Saturated hydrocarbons

Fredenhagen and Cadenbach determined equivalent conductivities of many substances, both organic and inorganic, over a range of dilution. Their results are summarized in Figure 1



Conductivities in Liquid Hydrogen Fluoride

It is apparent that the Λ_0 values fall in several ranges. These ranges correspond to the formation of various numbers of ions per molecule. Potassium fluoride and silver fluoride have nearly the same conductivities and are apparently completely dissociated into two ions, but potassium nitrate, and potassium acetate, both binary in water, apparently give four ions. Fredenhagen explains this by proposing the following:

$$KF \text{ ----- } K^+ + F^-$$
$$KNO_3 + 2HF \text{-----} K^+ + H_2NO_3^+ + 2F^-$$
$$HNO_3 + HF \text{ ----- } H_2NO_3^+ + F^-$$

Water gives two ions which are shown to be from the following reaction:

$$H_2O + HF \text{-----} H_3O^+ + F^-$$

The conductivity of H_2SO_4 is slightly greater than that of water and has been explained by the following:

$$H_2SO_4 + HF \text{ -----} HSO_3F + H_3O^+ + F^- ,$$

the HSO_3F being slightly dissociated.

Alcohols act as binary electrolytes; two theories to account for this have been proposed; either a fluoride and water are formed, or a proton is added to the alcohol and a fluoride ion formed. The latter is more probable. The same process holds in general for other organic substances. Specific groups

such as O^-, S^-, N^-, or $^-C{=}C^-$ must be present in the organic molecule or ionization does not take place (15). Klatt, a student of Fredenhagen's, has investigated many organic systems (13,14,15, 16, 17, 19). A summary of the uses of HF in organic chemistry has appeared recently (20).

Acid-base theory is very helpful in explaining many of the observed reactions. For instance, trichloracetic acid is very slightly ionized in hydrogen fluoride. In water it is a stronger acid than acetic; that is, it is a stronger donor and weaker acceptor. Thus it would have less tendency to take the proton in HF, hence its conductivity is less than that of acetic acid. Phenol is more acidic in water than is alcohol; hence it is a weaker acceptor and should be a poorer conductor in hydrogen fluoride than ethyl alchol. This is the case.

A comparison of the three solvents, ammonia, water, and hydrogen fluoride shows that ammonia is more basic than water as water adds a proton to ammonia, and water is more basic than hydrogen fluoride as water is the acceptor in this case. It is therefore to be emphasized that the nature of a polar solvent depends largely upon its acid-base properties. Hydrogen fluoride acts as a donor.

References

1. Fremy: Ann. Chem. phys., (3) 47, 5 (1856)
2. Simons: Inorganic Synthesis, Vol. I, 134, McGraw Hill 1939
3. Gore: Phil. Trans, 159, 173 (1869)
4. Fredenhagen and Dahmlos: Z. anorg. allgem. chem., 178, 272 (1928
5. Fredenhagen and Cadenbach: ibid., 178, 289 (1929)
6. Fredenhagen and Cadenbach: Z. physik. Chem., 146, 245 (1930)
7. Fredenhagen: Z. Electrochem., 37, 684 (1931)
8. Simons: Chem. Reviews, 8, 213 (1931)
9. Fredenhagen, Cadenbach, and Klatt: Z physik. chem., A164, 176 (1933)
10. Fredenhagen, Klatt, and Kunz: Z anorg. allgem. Chem., 218, 161 (1934)
11. Fradenhagen: Z physik. chem., B40, 51 (1938)
12. Fredenhagen and Cadenbach: Z anorg. allgem. Chem., 243, 39(193
13. Klatt: Z. physik. chem., A 173, 115 (1935)
14. Klatt: Z. anorg. allgem chem., 222, 225 (1935)
15. Klatt: ibid., 222, 289 (1935)
16. Klatt: ibid., 233, 307 (1937)
17. Klatt: ibid., 234, 189 (1937)
18. Franklin: Z.anorg. chem., 46, 3 (1905) footnote
19. Klatt: Z. physik. chem., A-185, 306 (1939)
20. Wiechert: Die Chemie, 56, 333 (1943)

Oxidation States of Copper

Henry Holtzclaw December 18, 1945

I. Introduction

The three elements copper, silver, and gold, are each known to have three oxidation states, +1, +2, and +3. The oxidation states of silver were discussed by Professor John C. Bailar, Jr., at a University of Illinois Inorganic Seminar in 1944 (3), the material being published later in the same year (4). In the case of copper, oxidation states of +1 and +2 are well recognized. A few textbooks mention trivalent copper briefly. Caven and Lander, "Systematic Inorganic Chemistry" (7), and Latimer, "Oxidation States" (14), each have one sentence on trivalent copper. Treadwell and Hall, "Analytical Chemistry" (22), devote a paragraph to the subject. A majority of textbooks omit mention entirely. This discussion concerns trivalent copper, principally.

II. Summary of Early Work

Krüger (10) first noticed the existence of trivalent copper and, in 1844, reported preparation of a compound of trivalent copper by oxidation of cupric hydroxide with chlorine. Fremy (9), in the same year, reported unsuccessful attempts to obtain trivalent copper compounds by allowing cupric hydroxide to react with potassium hypochlorite, and by fusing brass with potassium nitrate. Crum (8), in 1845, used bleaching powder upon a mixture of cupric hydroxide and cupric nitrate and reported the analysis of the product to correspond approximately to the formula Cu_2O_3. Krüss (11), forty years after Fremy's work, revived the work, fusing cupric hydroxide with a large amount of potassium hydroxide, and also cupric oxide with potassium perchlorate, dissolving the product of the reaction, in each case, in ice cold water. He obtained similar results when he decomposed copper peroxide (CuO_2) with boiling water. Vitali (23) reported, in 1894, formation of an oxide of trivalent copper by reaction of sodium hypobromite and cupric hydroxide.

Kuzma (12), in working on a new method of separation of tellurium from copper, antimony, and bismuth, noticed that during oxidation of tellurous acid to telluric by means of potassium persulfate, the solution turned intensely purple when traces of copper were present. This led Brauner (5) to suggest that the purple color might be due to formation of a compound of trivalent copper, whereupon Kuzma studied the problem further, obtaining compounds analyzing

$Cu_2O_3.CuO.2TeO_3.2K_2O.xH_2O$

(or) $2Cu_2O_3.CuO.3TeO_3.2K_2O.xH_2O$

Only in one case was the copper all trivalent:

$2Cu_2O_3.3TeO_3.2K_2O.13H_2O$

Kuzma felt that the salts were salts of complex copper-telluric acid.

Mawrow (18), in 1900, and Moser (19), in 1907, oxidized copper salts with hypochlorites and hypobromites, obtaining products which contained only very small quantities of active oxygen, probably because compounds were analyzed after partial decomposition by drying. Müller (20), in 1907, reported obtaining a brownish-red precipitate both of oxidation by cupric hydroxide with chlorine in a strong potassium hydroxide solution, and by the interaction of hypochlorites or hypobromites on metallic copper, or on cupric hydroxide. Together, Müller and Spitzer (21) followed this work with further experiments the same year proving the trivalency of copper and showing the ratio of copper to oxygen to correspond to Cu_2O_3 in a product obtained by anodic oxidation of copper in concentrated solutions of potassium or sodium hydroxide.

III. Work of Vrtis on Composition of Trivalent Copper Compounds

a. Preparation and analysis of compounds:

Vrtis became interested in establishing the composition of the complexes containing the trivalent copper. He prepared his solutions according to two methods:

1. Oxidation with potassium persulfate: An excess of telluric acid was added to the solution of cupric sulfate and warmed with potassium hydroxide and persulfate on the water bath. If the ratio of telluric acid to cupric sulfate was low, a reddish-brown precipitate occurred. If an excess of telluric acid was used, a clear, deeply purple solution resulted, without any precipitate.

2. Anodic oxidation: The anode was a platinum cup, plated with copper, and filled with a solution of potassium tellurate and hydroxide. The cathode was platinum, dipped in a diaphram containing potassium hydroxide solution. A high current density favored immediate formation of the purple trivalent copper solution. Vrtis used the anodic oxidation method, principally, to eliminate reaction products formed by the oxidizing agents.

Vrtis carried out analysis of the products by titration of the active oxygen with hydrogen peroxide and gravimetric determination of copper as the sulfide. The amount of trivalent copper was calculated from the value of active oxygen. Solutions prepared by either persulfate or anodic oxidation contained 95.8 to 98.1% of the copper in trivalent form. Those containing persulfate were more stable than those produced by anodic oxidation. Total decomposition took place after one to two weeks. A rise in temperature favored decomposition; cooling favored stability.

A number of experiments were carried out substituting other bases in place of the potassium hydroxide, and hypochlorite in place of persulfate, with varying success.

Investigation was made of the importance of the tellurate in the reaction by carrying out the anodic oxidation without the tellurate, followed by dipping the anode deposit into a solution of tellurate. The tellurate, apparently, is not necessary for formation of the trivalent copper compounds but does accomplish two things:

1. Solution of the trivalent copper precipitate through peptization, due to the tendency to form complexes:

$$KOH.Cu(OH)_3.nK_2TeO_4.Te(OH)_6$$

(n exceeding five in the case of the tellurates and one in the case of the periodates).

2. Increase of stability of the trivalent copper because of the high degree of oxidation of the tellurate.

Periodates were found to fulfil the same conditions as tellurates. The compounds obtained, using periodate instead of tellurate, contained 96.5 to 98.2% of the copper in the trivalent form.

The trivalent copper solutions proved to be colloidal when investigated ultramicroscopically. When spectroscopically analyzed, the solutions gave no selective absorption band, showing only continuous absorption in the violet region, a phenomenon characteristic of colloids.

b. Determination of composition of compounds:

Potentiometric determinations were made, in order to determine the composition of the trivalent copper compound. A copper electrode in solutions containing trivalent copper has a potential, due to the electrochemical process:

$$e^- + Cu^{+++} \longrightarrow Cu^{++}$$

Thus, the half-reaction e.m.f. is given by the relation:

$$\pi = \frac{RT}{nF} \ln \frac{[Cu^{+++}]}{[Cu^{++}]} + K$$

By considering the relation of all the ions present:

$$[K^+]^p \; [Cu^{+++}]^q \; [OH^-]^r \; [TeO_4^=]^s = \text{const.}$$

and by varying the concentration of one component, keeping those of the others constant, calculation could be made of the number of ions combined with one copper ion. The value obtained was greater than 3.5. The concentration of tellurate ions was found to have no influence upon the concentration of the trivalent copper ions. The concentration of hydroxyl ions had an inconsistent effect, which might be explained by the variability of the potential $Cu---Cu(OH)_2$ found by Allmand (19,20). The concentration of the trivalent copper ions was found to be indirectly proportianal to that of the potassium ions. The fact that the potential of the electrode depends upon the concentration of the potassium ion shows that potassium is a constituent of the trivalent copper compound. The formula $KCuO_2$ would explain behavior of the electrode, by decomposition. The stoichiometric composition is, apparentl nearest to the formula $KCu(OH)_4$.

$[Cu^{++}][OH^-]^2 = K$ $\qquad$ $[Cu^{++}][OH^-]^2 = K$

$[Cu^{++}] = \dfrac{K}{[OH^-]^2}$ $\qquad$ $[Cu^{++}] = \dfrac{K}{[OH^-]^2}$

Subst. in $\pi = \dfrac{RT}{n'v} \ln \dfrac{[Cu^{++}]}{[Cu^{++}]} + K$

$= \dfrac{RT}{n'v} \ln \dfrac{K}{K} [OH^-]^{2-2} + K$

where $y > 3.5$ and

$\therefore$ K Cu(OH)$_2$ ignored.

Trivalent copper hydroxide is an acid and, thus, bears out the theory that the basicity of an oxide decreases with increase in oxidation number. Cu_2O is a definite base, $Cu(OH)_2$ is less basic, and $Cu(OH)_3$ is on the acid side.

IV. Summary of Work since 1925

In 1935, Buntin and Vlasov (6) dissolved freshly precipitate cupric hydroxide in excess 34% sodium hydroxide solution and treated the resulting solution with $NaHO_2$. A violent reaction, for which the temperature must be controlled, ensues, resulting withing ten to fifteen minutes in a red precipitate of Cu_2O_3. The yield, based on $NaCuO_2$, is 80 to 90%. With sulfuric acid, the Cu_2O_3 does not give hydrogen peroxide and is, therefore, a true oxide. In the presence of nitric acid, the compound oxidized oxalic acid to carbon dioxide and water. These experimenters substantiate the work of Vrtis on stability, by showing that the compound is quite unstable at elevated temperatures.

Malatesta (15,16,17), in 1941 and 1942, worked on preparation of pure trivalent copper and trivalent silver tellurates and periodates. The periodates of trivalent copper were of the composition $M_7^+Cu^{+++}(IO_6)_2.nH_2O$. The trivalency in such complexes in indicated by the method of preparation, their chemical properties, their magnetic susceptibilities (compounds are diamagnetic), and by the fact that the corresponding gold compound can be prepared directly from a salt of trivalent gold. The compound $K_7CuI_2O_{12}.7H_2O$ was prepared as follows:

a. Filter a mixture of potassium periodate (23 grams), aqueous potassium hydroxide (27 grams in 70 cc), and fresh cupric hydroxide (0.05 M).

b. Electrolyze in a porous cell containing 10% aqueous potassium hydroxide (10cc) with a Winkler screen anode and a platinum wire cathode and current of one ampere for two hours.

c. Evaporate in vacuo.

d. Filter and wash residue with ethyl alcohol.

e. Dissolve in minimum of water and repeat the operations.

The compound is emerald green; its aqueous solutions are brown; and it is decomposed by acids with evolution of oxygen.

Malatesta prepared tellurates of trivalent copper and of trivalent silver, of general composition $M_9^+ M^{+++} (TeO_6)_2.nH_2O$, in a way analogous to the preparation of the periodates. $Na_5H_4Cu(TeO_6)_2.18H_2O$ is a maroon red compound which, with 20% aqueous sodium carbonate, can be changed over to another form, $Na_7H_2Cu(TeO_6)_2.12H_2O$, dark chestnut red, insoluble in dilute aqueous sodium carbonate. In aqueous solution, the second form is slowly transformed into the first.

V. Conclusion

Enough work has been done on compounds of trivalent copper to prove their existence and something of their composition and properties. Although the field seems to show considerable promise of new compounds, recent work is somewhat lacking.

BIBLIOGRAPHY

1. Allmand, J. Chem. Soc., 95, 2151 (1909).
2. Allmand, ibid, 97, 603 (1910).
3. Bailar, Inorganic Seminar, Univ. of Ill. (1944).
4. Bailar. J. Chem. Ed., 21, 523 (1944).
5. Brauner, Ber., 40, 3362 (1907).
6. Buntin and Vlasov, Acta Univ. Voronegiensis, 8, No. 4, 6-11 (1935)
7. Caven and Lander, "Systematic Inorganic Chemistry", p. 113 (1930).
8. Crum, Ann., 55, 213 (1845).
9. Fremy, Ann. chim. phys., (3), 12, 457 (1844).
10. Krüger, Ann. Phys. (Pogg.), 62, 447 (1844).
11. Krüss, Ber., 17, 2593 (1884).
12. Kuzma, Rozpr. c. ak. tr. (2), 10, 31.
13. Kuzma, ibid, (2), 14, 11.
14. Latimer, "Oxidation States", p. 169 (1938).
15. Malatesta, Chem. Zentr. 1942, I, 2114-5.
16. Malatesta, Gazz. chim. ital., 71, 467-74 (1941).
17. Malatesta, ibid, 71, 580-4 (1941).
18. Mawrow, Z. anorg. Chem., 23, 233 (1900).
19. Moser, ibid, 54, 121 (1907).
20. Müller, ibid, 54, 417 (1907).
21. Müller, and Spitzer, Z. Electrochem., 13, 25 (1907).
22. Treadwell and Hall, "Analytical Chemistry", I, p. 113 (1921).
23. Vitali, Bull. chim. pharm., 38, 668 (1894).
24. Vrtis, Rec. trav. chim., 44, 425-434 (1925).

The Production of Aluminum

John C. Bailar, Jr. _ January 8, 1946

Although aluminum is the most abundant metal in the earth's crust and occurs in many minerals, practically all of it is produced from one ore--bauxite. This is essentially $Al_2O_3 \cdot 2H_2O$, but it always contains some ferric oxide and varying amounts of silica. Practically all aluminum of commerce is obtained by purifying the ore by the Bayer process and reducing it by the Hall-Heroult process. The Bayer treatment is applicable only to low silica bauxites, which are not abundant or widely distributed. Many countries (i.e. Germany and, to some extent, the United States) have therefore become dependent upon imported ore. A tremendous amount of work has been done upon methods of obtaining aluminum from high silicate bauxite or other ores, but most of it has not found its way into the chemical journals, and is not even mentioned in the text books. It is to be found in the patent literature.

The methods of attacking this problem fall into two classes--those which modify the Bayer process, and those which approach the matter from entirely different points of view.

Modifications of the Bayer Process

A. Beneficiation of the ore by washing, flotation, or other mechanical means. While this is sometimes effective in removing admixed silica, it is not applicable to silicate ores, and shows little promise. (1,2)

B. The lime-soda sinter process. (1,3). When bauxite is digested with sodium hydroxide, any silica which is present precipitates as $Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 9H_2O$ or some similar compound so that each pound of silica holds 1-2 lbs. of alkali and a similar amount of alumina. Titanium exerts a similar effect. If the ore contains more than 6-7% silica, it cannot be treated economically by the Bayer process. The lime-soda sinter involves sintering with limestone and soda to give insoluble calcium aluminate, dicalcium silicate and unchanged ferric oxide. The finely ground clinker will react with aqueous sodium carbonate to give sodium aluminate, the solution of which may be very highly concentrated. Many "red muds" have been put through this process in recent years. Modifications of this process are known as the "Pederson Process" and "Deville Process" The former has been put into operation in Europe.

C. Ferrosilicon Process (1) When a mixture of bauxite (or aluminosilicate) and iron oxide is heated with carbon and a limestone flux, the iron and most of the silicaon are reduced to ferrosilicon, and 95-98% of the aluminum remains in the slag as $Ca(AlO_2)_2$. This reacts readily with sodium carbonate to give $NaAlO_2$, which is treated as usual. The commercial development of this process depends upon the development of uses for ferrosilicon.

Other Methods

A. Acid decomposition (2) Most aluminosilicates are attacked by hot concentrated sulfuric acid, aluminum sulfate passing into solution. Crystallization removes impurities (Fe), after which the sulfate is thermally decomposed to oxide, the SO_3 being recycled. This process requires expensive materials of construction and does not give pure aluminum.

B. Ammonium sulfate decomposition (1,2,6). This is a variant of the above, ammonia being liberated during the initial heating process. The aluminum sulfate is crystallized as the ammonium alum and precipitated as the hydroxide by addition of the ammonia liberated in the initial digestion. The ammonium sulfate is recovered from the filtrate and recycled.

C. The Kalunite process (1). Alunite is a crude hydrated potassium aluminum sulfate which occurs in large amounts in several western states, particularly in Utah. After calcining, it is dissolved in water containing a little dilute sulfuric acid, and crystallized as the potassium alum. This is hydrolyzed to a basic alum which is thermally decomposed to K_2SO_4 and Al_2O_3, the SO_3 being used to decompose clay. For each ton of alunite, two to three tons of clay can be treated.

D. Ammonium Oxalate Method. The ore is digested under pressure with aqueous ammonium oxalate, the complex going into solution as $(NH_4)_3[Al\ Ox_3]$ and half of the ammonia escaping. The ammonium oxalate is recovered and the aluminum is precipitated by the action of ammonia. The reactions are said to go readily and to give excellent yields.

E. Chlorination (4) Many oxide and silicate ores can be converted to anhydrous chlorides by heating with chlorine or hydrogen chloride in the presence of carbon. Separations can be effected through the differences in ease of chlorination and in volalility of the resulting chlorides. Thus, ferric oxide is more easily formed than aluminum chloride and the reaction $AlCl_3 + Fe_2O_3 \longrightarrow FeCl_3 + Al_2O_3$ proceeds readily even below 200°C. Chlorination of ores has been studied, not only for aluminum, but for iron, nickel, manganese, chromium, tungsten and many other metals.

F. Hydrochloric acid extraction (5) The bauxite is dissolved in hot hydrochloric acid, and the silica is removed by filtration. The ferric chloride is extracted with butyl acetate or similar solvent.

G. Reduction by Carbon, Carbides, Hydrocarbons, etc. At sufficiently high temperatures, aluminum oxides and silicates can be reduced to metal, especially in the presence of excess iron oxide. This gives an alloy of iron, silicon and aluminum, frim which the aluminum is volatalized in vacuo (4mm. of mercury at 1250-1360°). Ferrous sulfide has also been suggested as the reducing agent (8) Matuura (9) has suggested adding copper compounds to the ore, and reducing the mixture with carbon. This gives an alloy of aluminum and copper, from which the aluminum is distilled.

I. <u>Boron trifluoride method</u> (10) At 450°, BF_3 reacts with many oxides and silicates.

$$2BF_3 + Al_2O_3 \text{ ----- } 2AlF_3 + B_2O_3 \rightarrow (BOF)_3$$

$$6BF_3 + 3SiO_2 \text{ ----- } 3SiF_4 + 2(BOF)_3$$

$$MSiO_3 + 3BF_3 \text{ ----- } MF_2 + SiF_4 + (BOF)_3$$

$$K\,AlSi_3O_8 + BF_3 \text{ ----- } AlF_3 + SiF_4 + (BOF)_3 + KBF_4$$

Most of the fluorides are volatile, but aluminum remains behind. Iron oxide also remains, as it is unattacked below 500°. No details are given for the treatment of the simplified mixture.

Bibliography

(1) Dean, Mining and Metallurgy 24, 356 (1943)
(2) Wilson, Mining and Metallurgy 24, 359 (1943)
(3) Pedersen, Ginsberg and Wrigge, Metal und Erz 41, 32 (1944)
(4) Lebedev, Moscow Institute in Honor of J. V. Stalin 1935, 5
Carl, U.S. Patent 2, 296, 422 (Sept. 22, 1942)
(5) Hixson and Miller, U. S. Patent 2, 249, 761 (July 22, 1941)
(6) Moss and Dye Australian Patent 111, 758 (Oct 8, 1940)
(7) Gentil, U.S. Patent 2, 294, 546 (Sept 1, 1942)
Armendias British Patent 532, 115 (Jan. 17, 1941)
Schlecht and Jahrstorfer U.S. Patent 2, 242, 759 (May 20,1941)
Clark, U.S. Patent 2, 297, 747 (Oct 6, 1942)
(8) Societe d'electrochimie. British Patent 523, 621 (July 18, 1940)
(9) Matuura Japanese Patent 137, 708 (Aug 2, 1940)
(10) Baumgarten and Bruns Ber. 74B, 1232 (1941).

Recent Developments in the Chemistry of Organic Phosphorus Dichlorides and Their Derivatives

Arthur Toy January 15, 1946

Introduction

The study of the chemistry of organic phosphorus chlorides constitutes a phase of the research program on organic and inorganic phosphorus compounds at the Research Laboratories of the Victor Chemical Works. The choice of the organic phosphorus chlorides as the parent compounds is due to the versatility of the reactive chlorine atoms from which many other compounds may be derived. Since there are a great many organic phosphorus chlorides, a discussion of each individual one would be too involved. Therefore a representative compound of this type was chosen for this discussion. This compound is the one which we have made readily available, phenylphosphorus dichloride or phosphenyl chloride, $C_6H_5PCl_2$. Some of the other organic phosphorus chlorides will also be mentioned in the discussion for specific illustrations.

1. Phenylphosphorus Dichloride

A. Preparation

1. $C_6H_6 + PCl_3 \xrightarrow{AlCl_3} C_6H_5PCl_2 + HCl$ (13)

2. $C_6H_6 + PCl_3 \xrightarrow{500-700°C} C_6H_5PCl_2 + HCl$ (10)

3. $2COCl_2 + C_6H_5PH_2 \longrightarrow C_6H_5PCl_2 + 2CO + 2HCl$ (12)

4. $PCl_3 + Hg(C_6H_5)_2 \longrightarrow C_6H_5PCl_2 + C_6H_5HgCl$ (6)

(Preparation of some other organic phosphorus chlorides):

1. $(C_6H_5)_2C{=}CH_2 + PCl_5 \longrightarrow C_6H_5)_2C\text{-}CH_2PCl_4$ (3)

2. $RCH{=}CH_2 + PCl_3 \xrightarrow[\text{peroxide}]{\text{diacetyl}} RCHCl\text{-}CH_2PCl_2$ (4)

B. Hydrolysis

$$C_6H_5PCl_2 + 2H_2O \longrightarrow C_6H_5P(=O)(H)(OH) + 2HCl \quad (5)$$

(white crystalline monobasic acid)

C. Esterification

1. With aliphatic alcohols (11)

$$C_6H_5PCl_2 + 2RONa \longrightarrow C_6H_5P(OR)_2 + 2NaCl$$

$C_6H_5P(OC_3H_7)_2$ b.p. 138-140° C at 4-5 mm.

2. With phenols

$$C_6H_5PCl_2 + 2ArOH \longrightarrow C_6H_5P(OAr)_2 + 2HCl$$

The trivalent phosphorus atoms in these neutral esters indicated that they may be useful as inhibitors, antioxidants, and oil-additives. Many such uses for the aromatic esters have appeared in the patent literature (14). All of these esters have a characteristic phosphinic odor.

D. Oxidation

1. Phenylphosphorus tetrachloride (10)

$$C_6H_5PCl_2 + Cl_2 \longrightarrow C_6H_5PCl_4$$

2. Phenylphosphorus oxydichloride (10)

a. Preparation

$$C_6H_5PCl_2 + O \longrightarrow C_6H_5POCl_2$$
$$C_6H_5PCl_4 + H_2O \longrightarrow C_6H_5POCl_2 + 2HCl$$
$$C_6H_5PCl_4 + SO_2 \longrightarrow C_6H_5POCl_2 + SOCl_2$$

b. Hydrolysis

$$C_6H_5POCl_2 + 2H_2O \longrightarrow C_6H_5PO(OH)_2 + 2HCl$$

(white crystalline dibasic acid)

c. Esterification

1) With aliphatic alcohols

a) $C_6H_5PO(OAg)_2 + 2CH_3I \longrightarrow C_6H_5PO(OCH_3)_2 + 2AgI$ (8)

b) $C_6H_5POCl_2 + 2ROH \longrightarrow C_6H_5PO(OR)_2 + 2HCl$

These esters are colorless liquids. With the exception of the lower esters, they are rather stable to hydrolysis by water. Their volatility is fairly low and the heat stability pretty high. Their properties are analogous to the aliphatic esters of phthalic acid which are widely used as plasticizers. The phosphonates have the additional advantage over the phthalates in that they impart some fire-proofing characteristic to the resin they plasticize. Formerly aromatic phosphates such as tricresyl and triphenyl phosphates were used as fireproofing plasticizers. However, these aromatic esters have several weak points: (a) poor light stability, and (b) low temperature flexibility. For example, vinylite sheets plasticized with alkyl esters of phosphonic and phosphoric acids will remain flexible at temperatures as low as -40 to -50° C while similar sheets plasticized with aromatic phosphates become brittle at around -4 to -5° C.

2) With phenols (7)

$$C_6H_5POCl_2 + 2ArOH \longrightarrow C_6H_5PO(OAr)_2 + 2HCl$$

These esters are similar to the triaryl phosphate Many of them have been evaluated as plasticizers.

3. Phenylphosphorus thiodichloride

a. Preparation

$$C_6H_5PCl_2 + S \xrightarrow{160^\circ C} C_6H_5PSCl_2 \qquad (9)$$

b. Hydrolysis

Decomposes in water. Pure $C_6H_5PS(OH)_2$ has never bee isolated.

c. Esterification

1) With aliphatic alcohols

No pure aliphatic esters have been prepared

2) With phenols

$$C_6H_5PSCl_2 + 2C_6H_5OH \longrightarrow C_6H_5PS(OC_6H_5)_2 + 2HCl$$

When the reaction was first carried out by heating the mixture at refluxing temperature, it proceeded very slowly. Several drops of PCl_3 were then added as catalyst. This catalyst was first discovered in this laboratory for the synthesis of $(C_6H_5O)_3P{=}S$ by the action of $PSCl_3$ on C_6H_5OH (2). The probable mechanism involved may be illustrated by the following equations:

$$PCl_3 + 3C_6H_5OH \longrightarrow (C_6H_5O)_3P + 3HCl$$
$$(C_6H_5O)_3P + C_6H_5PSCl_2 \longrightarrow (C_6H_5O)_3PS + C_6H_5PCl_2$$
$$C_6H_5PCl_2 + 2C_6H_5OH \longrightarrow C_6H_5P(OC_6H_5)_2 + 2HCl$$
$$C_6H_5P(OC_6H_5)_2 + C_6H_5PSCl_2 \longrightarrow C_6H_5PS(OC_6H_5)_2 + C_6H_5PCl_2$$

As can be seen from the equations, the real active catalyst is $C_6H_5PCl_2$. In the actual experiments it was found that in the absence of the catalyst after ten hours, 66% of the theroetical HCl was collected while in the presence of 0.5% of PCl_3, 91.7% of HCl was collected after only three hours of heating.

Organic Phosphorus Polymers

In the duscussion on the esters of phosphonic acids, some emphasis was placed on the fact that they are good plasticizers, and that they impart fireproofing properties to the resins plasticized. An ideal situation would be the synthesis of a phosphorus-containing resin. Such a resin, among other things, would be non-flammable by itself without the addition of an external agent.

The only well known phosphorus-containing polymer is the polymeric $PNCl_2$. (1) This polymer has a tendency to depolymerize and also to liberate HCl in the presence of atmospheric moisture.

We have attempted to obtain polyesters by reacting the phosphorus trichlorides with dihydroxy compounds. However, due to the trifunctional characteristic of the trichlorides, only an infusible and insoluble mass was obtained. Even the reaction of such compounds as $C_6H_5OPOCl_2$ with dihydroxy compounds failed to yield any fusible or soluble polymers. This was due to the liberation of $POCl_3$ from $C_6H_5OPOCl_2$ under the influence of heat from probably the following equilibrium:

$$C_6H_5OPOCl_2 \xrightarrow{\Delta} (C_6H_5O)_2POCl + (C_6H_5O)P{=}O + POCl_3$$

With the advert of the organic phosphorus dichlorides in which the organic radical is attached firmly to the phosphorus atom by C-P bond, a new field was opened up for research on phosphorus polymers. From a portion of our research projects we have been able to obtain some very interesting phosphous thermoplastic as well as thermosetting polymers.

A. Thermoplastic Phosphorus Polymers

These are polyphosphonates. They are linear polymers of large molecular weight.

Properties: 1. Non-flammable

2. May be drawn from molten state into fibers with cold drawing property.

3. Soluble in some organic solvents, and the solution usable as transparent lacquer.

4. Varies from brittle solid to very tough and strong horny solid depending on degree of polymerization and composition.

5. Light yellow to dark amber color

B. Thermosetting Phosphorus Polymers

These polymers are obtained from the catalytic polymerization of the unsaturated organic phosphorus monomers.

Properties: 1. Solid transparent plastic.

2. Refractive index around 1.58.

3. Water-white to light yellow.

4. Flame resistant.

5. High heat distortion temperature.

6. More scratch resistant than commercial thermoplastics.

7. Insoluble in organic and inorganic solvents.

The monomers may also be copolymerized with some commercially available thermoplastics to convert them into thermosetting resins and to impart to them the desirable properties listed for the pure phosphorus polymers.

Conclusion

This brief discussion on some phases of the chemistry of organic phosphorus dichlorides indicates that the field of organic phosphorus chemistry is varied and extensive. Many valuable derivatives with properties inherent to the phosphorus atom have been discovered. However, we have merely touched the field. The extensiveness of this field is certainly a challenge to any research chemist.

Biobliography

1. Audrieth, Steinman, Toy, Chem. Rev. 32, 109 (1943)
2. Gottlieb, J. Am. Chem. Soc. 54, 748 (1932)
3. Harnist, Dissertation, Strassburg, pp. 1-48 (1910)
4. Kharasch, Jensen, Urry, J.Am.Chem.Soc. 67, 1864 (1945)
5. Michaelis, Ananoff, Ber. 7, 1688 (1874)
6. Michaelis, Graeff, Ber. 8, 922 (1875)
7. Michaelis, Kammerer, Ber. 8, 1306 (1875)
8. Michaelis, Benzinger, Ber. 8, 1310 (1875)
9. Michaelis, Kohler, Ber. 9, 1053 (1876)
10. Michaelis, Ann. 181, 265-365 (1876)
11. Michaelis, Kohler, Ber. 10, 816 (1877)
12. Michaelis, Dittler, Ber. 12, 338 (1879)
13. Michaelis, Ber. 12, 1009 (1875)
14. U.S.P. 2,274,291 and 2,174,019 (1942) and (1939)

Some Studies On the Plating Of Cobalt and Nickel From Coordination Compounds

Margaret Kramer January 22, 1946

Introduction

Coordination compounds have long been used in electroplating bath because experience has shown that such complexes are effective in producing smooth plates and are quite useful for plating alloys.

The constituents of electroplating baths have been chosen largely by trial and error, and not as the result of systematic studies of the role of coordination compounds as electroplating agents. Recently, however, at least one author has stressed the study of cyano complexes as examples of Werner complexes (1).

In addition to their use as sources of metal ions, coordination compounds have been thought by some to be the key to the effectiveness of addition agents (2). Such an hypothesis of the nature of addition agents has not been subjected to systematic study.

There is little variety in the types of complexes used by industry for plating. The major use of coordination compounds to date has been the use of the cyano complexes in the plating of copper, zinc, cadmium, gold, silver, and brass. Perhaps the lack of a study of electroplating agents as examples of Werner complexes has retarded the development of other types of baths.

The study reported in this particular discussion was undertaken in an attempt to determine whether some property or properties of a complex were important in characterizing the plating ability of that complex.

A variety of stable cobaltic ammines is available for a study such as this. Later some of the few stable cobaltous ammines were used.

Since nickel ammines also are generally stable in solution, and since nickel plating, unlike cobalt electroplating, is commercially important, nickel ammines were chosen for additional investigations.

Experimental

Many of the compounds of cobalt studied were available from laboratory stock; others were made according to methods found in the literature. All of the nickel ammines studied were prepared by methods outlined in the literature.

Preliminary plating tests were run on the cobaltic complexes, using 0.5% solutions, platinum anodes, and varying current densities. Tests on the nickel complexes were done in the same fashion, but using nickel anodes and 1% solutions.

As a result of these plating tests, the complexes were classified according to their plating ability as good, fair, or poor. Examples of each type follow.

Good: $[Coen_3]Cl_3$, $[Nien_3]Cl_2$

Fair: $[Co(NH_3)_4CO_3]_2SO_4$, $[Coen_2Cl_2]Cl$, $[Nipn_3]Cl_2$, $[Nibn_3]Cl_2$

Poor: $[Co(NH_3)_6]Cl_3$, $[Copy_4Cl_2]Cl$, $[Nipy_4]Cl_2$, $Ni(stien)_2]Cl_2$, $[Ni(dip)_3]Cl_2$

All of the ammonia derivatives containing nitro groups were poor plating agents. An example of this type is $NH_4[Co(NH_3)_2(NO_2)_4]$.

The change of pH during plating was studied, using 0.5% solutions and a current of 0.2 ampere for 20 minutes. The change in pH is apparently not an important factor in producing good plates, for complexes producing good plates showed the same sort of pH changes as those producing poor ones. Fluoborate was found to be an excellent buffer for nickel plating baths, a comple such as $[Nien_3](BF_4)_2$ showing little or no change in pH during plating.

Current efficiency studies were made on many of the baths. In the case of $[Coen_3]Cl_3$, it was found that cobalt plates from the trivalent state but dissolves from the anode in the divalent condition. We were not able to find a coordinating agent which would allow the cobalt to dissolve from the anode in the trivalent state. There is evidence that $[Coen_3]Cl_3$ is regenerated in the bath, the $[Coen_3]^{++}$ ion which is probably first formed being oxidized by air to $[Coen_3]^{+++}$.

A bath containing $[Nien_3]^{++}$ and some excess ethylenediamine gave cathode efficiencies of 90% or above. This bath is being studied further.

Discussion

The data collected during this study indicate definitely the effect of stability of the complex and the effect of steric hindrance offered by the coordinating amine to the metal ion during plating. It has been found that an ammine of intermediate stability toward reduction is better for producing a plate than a very stable one or a very unstable one. It has also been found that large organic groups can so shield a metal ion that the plate produced is progressively poorer as the size of the substituent group increases.

Using half-wave potentials (3,4) as a measure of stability toward reduction, it is found that complexes with potentials more negative than about -0.75 v. are poor or non-plating agents; complexes with half-wave potentials between -0.70 v. and -0.50 v. are generally good plating agents; while those with half-wave potentials less negative than about -0.50 v. are poor plating agents. In each case, the exceptions to this generalization are ethylenediamine complexes. This leads to the supposition that stability is not the only factor.

As a result of studying a series of substituted ethylenediamines as coordinating agents, it was found that the size of the coordinating group is important. The effect of stability cannot be neglected here, however, for stability usually decreases with increasing weight of the amine. Moreover, the diamines can achieve stability through chelation, whereas a coordinating group like pyridine cannot.

The progressively poorer plating character as the size of the substituent group increases is partially a steric effect. Substituent groups actually serve to hinder the plating of the metal ion.

Further data are needed to establish the bounds of stability and the limits of substitution more exactly.

The actual mechanism by which a complex accepts electrons becomes important; for if the metal plates directly from the complex rather than from the aquated ion, some of the coordinating amine might be included in the plate. This inclusion may account for the non-adherence of some of the plates. We have been able to detect nitrogen in plates from a cobaltic pyridine complex and from the hexammino cobaltic ion, but we have not found it in the plates from a cobalt-ethylenediamine bath. These data are too incomplete to permit drawing any conclusions.

Summary

1. A series of cobaltic ammines and one of nickelous ammines, together with a few cobaltous ammines, have been studied from the point of view of their function as electroplating agents.

2. It is suggested on the basis of the data collected that stability of complex ions and character of the coordinating group are decisive factors.

3. The ability of coordination compounds containing substituted ethylenediamines to produce good plates decreases with increasing size of the coordinating group.

4. Stability of the complex ion is an important factor for the ammonia derivatives as well as for the ethylenediamine derivatives. A compound may be too stable toward reduction or too unstable to plate satisfactorily.

5. Within the limits of the data collected, we have not been able to demonstrate that pH is an important factor in the formation of a good plate.

6. Fluoborate has been found to be superior to pyrophosphate as a buffer in the nickel plating baths of the type used in this study.

Bibliography

1. Thompson, Trans. Electrochem. Soc. 79, 417 (1941)
2. Fuseya and Murata, ibid 50, 235 (1926)
3. Herda, Thesis, University of Illinois, 1943, p. 24
4. Willis, Friend, and Mellor, J. Am. Chem. Soc. 67, 1680 (1945)

$[NH_4][Co(en)_2(NO_2)_2]$

$[Co(en)_2(NH_3)_2]^{+}$

$[Co(en)_4]ClO_4$

$[Co(en)_2]Cl_2$

$[Co(en)_3]Cl_3$

$[Co(en)_2Cl_2]Cl$

$[Co(en)_4Cl_2]Cl \cdot 6H_2O$

Electronic Quantum States of Atoms and Molecules

H. A. Laitinen January 29, 1946

Quantum mechanics has provided an exact interpretation of the possible quantum states of a single electron in a hydrogen-like atom or ion, but not in general for multiple-electron atoms or molecules. On the other hand, spectroscopy is an elegant method for the experimental determination of energy states of electrons in simple or complex atoms or molecules. The theoretical explanation of the energy states of complex systems in only approximate, and is essentially an expansion of concepts well established for simple systems to account for experimental observations on complex ones.

A. Quantum States of Single-electron Systems

One-electron systems such as H, He^{+}, Li^{++} etc. can be exactly described by a system of four quantum numbers. The energy of an electron is defined by just two quantum numbers (n and ℓ) for such simple systems in the absence of an electric or magnetic field.

The important energy states of atoms like Na, K, or ions like Ca^{+}, Sr^{+}, Al^{++} can be accounted for in a similar manner, since they are essentially one-electron systems with a diffuse central charge, which acts to separate the energy levels of a given n but different ℓ value.

B. Interaction of two or more electrons in Single Atoms

In accordance with the Pauli exclusion principle, a many-electron system can be resolved into a series of closed shells of equal n, and subshells of equal ℓ values.

A detailed consideration of energy levels requires an examination of the victor summation of angular momenta of the various electrons, both with regard to spin and orbital motion. The various spin contributions are added to give a resultant S and the orbital momenta to give a value L for the atom. The S and L values combine to give a resultant J which describes the total angular momentum due to electrons. Adding the nuclear spin I gives F, the total for the atom. At each step of the summation the resultant as well as the components are quantized.

The spectroscopic "term" or energy state designation gives the values of S, L and J in a short hand fashion. The following generalizations are often helpful:

1. A closed shell always forms a $^1S_0$ state, indicating a zero resultant electron spin (paired electrons) and zero L value.

2. The principal quantum number n does not determine the spectroscopic term. Thus atoms in the same periodic family usually have the same term in the ground state.

3. For a given subshell (ℓ value) the term for q electrons is the same as for r-q electrons, where r is the maximum number of electrons in the subshell, that is $2(\ell + 1)$. For example, there are 6 possible p electrons, and the same spectroscopic term arises for 6 or 0, 5 or 1 and 4 or 2 electrons.

4. The lowest energy state (ground state) of the terms given by equivalent electrons (same n and ℓ), is that of the greatest multiplicity. Of terms of equal multiplicity the term of greatest L has the lowest energy. (Hund Rule). Thus of the terms of ^1S or ^1D, or ^3P or ^3F the latter has the lowest energy.

5. A regular multiplet is one in which the energy increases with increasing J, and an inverted multiplet is the opposite. For a given sub-group (equivalent electrons), the multiplet is regular when less than half of the shell is occupied, and inverted when more than half is occupied. Since the stable ground state is that of lowest energy, this rule is of great importance in describing the magnetic properties of groups of elements like the rare earths.

C. Quantum States of Molecules; Molecular Orbitals

The present discussion is limited to the ground state and activated electronic states of diatomic molecules. For each electronic state there are a series of robational and vibrational energy states which are not considered. Fundamentally, the electronic states of molecules can be derived in three ways: (a) bringing together the atoms, (b) splitting the united atom, thus coming from zero nuclear separation, (c) adding electrons one by one to the nuclei, in an analogous fashion to building up atoms. To emphasize the analogy between atomic and molecular orbitals, the latter two concepts are considered here.

1. The system: 1 electron, 2 nuclei

Stationary energy states can be characterized by three quantum numbers (disregarding electron spin), as in atoms. However, only one quantum number can be precisely defined for all separations of the nuclei. This is λ, the component of the orbital angular momentum along the internuclear axis, corresponding to ℓ for atoms. The other two quantum numbers can be defined only approximately and in two ways depending on whether the nuclear separation is very small or very large. For small separations, the molecule acts like an atom in an electric field, while for large separations the electron is associated either with nucleus A or nucleus B, with an electric field produced by the other nucleus. For actual nuclear separation, a correspondence is recognized between orbitals for small and large separation, and the energy state is intermediate between the two extremes.

2. The system: several electrons, 2 nuclei

The Pauli exclusion principle holds for molecular orbitals just as it does for atomic ones. As a combined atom is split, and the separation increases the quantum numbers n and ℓ lose more and more of their significance, but the number of states is not affected.

The spectroscopic terms of molecules are derived in a fashion analogous to that used for atoms, with Greek letters replacing the Latin for each designation. A $^1\Sigma$ molecular state corresponds to a ^1S atomic state. As with atoms, the state with the greatest multiplicity lies deepest.

D. Selected Applications of inorganic interest.

1. Reaction of H_2 with Cl_2

The Cl_2 molecule absorbs light and splits into atoms, one of which is in the ground state ($^2P_{\frac{1}{2}}$) and the other in an excited state ($^2P_{\frac{3}{2}}$). The excited atom (excitation energy 2.5 kcal.) can react with H_2 to give HCl and H, but with the normal atom the reaction is endothermic to the extent of about 1 kcal.

2. The molecule He_2

This molecule can not exist in the ground state, but can exist in excited states, for example in electric discharges. This stability can readily be understood from molecular orbitals. The limiting case of the ion He_2^+ is also stable.

3. The molecule O_2

The molecular orbital picture explains the paramagnetism of molecular oxygen in its lowest energy state.

References

1. Herzberg, "Atomic Spectra and Atomic Structure", Dover Publications, New York, 1944
2. Herzberg, "Molecular Spectra and Molecular Structure, I. Diatomic Molecules", Prentice -Hall, Inc., New York, 1939. Chapt V, VI, VIII.
3. Palmer, "Valency, Classical and Modern", Cambridge University Press, London 1945)

INDUSTRIAL PREPARATION AND USES OF THE RARE EARTHS AND THORIUM

Howard E. Kremers March 19, 1946
Lindsay Light and Chemical Company

The rare earths and thorium are usually obtained commercially from monazite sand. Monazite is essentially a phosphate of the rare earths and thorium. The industrial preparation of the rare earths involves (1) the isolation of purified thorium, cerium, lanthanum, neodymium and praseodymium compounds and (2) the removal of non-rare earth impurities such as silica, phosphates, iron, etc. Both types of processes are complicated by the fact that expensive reagents such as oxalic acid cannot be used unless economic or purity conditions warrant such use.

Although thorium is not a rare earth, its separation from the rare earths is usually a rather tedious process. When starting with monazite sand, two types of initial treatment are possible. One kind of treatment leaves the thorium as an insoluble material, while the rare earths are left in a soluble form. The other method gives a material in which both thorium and the rare earths are soluble. The particular thorium process chosen for use, however, can be essentially the same for both kinds of treatment.

Cerium is the most important of the rare earths. It can be separated from the latter in rather pure form by a modification of fractional basic precipitation after oxidation of the cerium to the ceric state.

Cerium-free rare earths (commercially known as "didymia") are separated into individual rare earths wherever possible by fractional crystallization methods. In large scale work, a continuous fractional crystallization scheme is used.

Valuable by-products of monazite working are mesothorium, europium, and yttrium earth concentrates. These are recovered when the demand is great enough.

The principle use of thorium is still in the manufacture of incandescent mantles. Thorium and lanthanum are used in special optical glasses for making lenses with high resolving power at large aperatures.

The principle use of cerium and rare earth mixtures is in the glass industry. Cerium replaces arsenic as a glass decolorizer and didymium acts as a physical decolorizer. A specially prepared ceric oxide is replacing rouge in precision optical polishing. Ceric oxide shows promise as an opacifier in vitreous enamels. Considerable quantities of rare earth oxide and rare earth fluoride are used in cored carbons for arc lighting.

General references: U. S. Patents: 1,087,099 1,881,126
1,366,128 1,182,880
1,069,959 1,335,482
British Patents: 129,624
510,198
120,748

Eu recovery: H. N. McCoy: J. Am. Chem. Soc., 58, 2279 (1936)
Y-earth recovery: Moeller and Kremers: Ind. Eng. Chem., Anal. Ed., 17, 44 (1945).

ISOSTERISM IN INORGANIC COMPOUNDS

G. K. Schweitzer April 2, 1946

I. Introduction

The outer sphere (1) of an atom seems to control its valency. The chemical behavior of an element is controlled by two factors:

1. The surplus nuclear charge (the atomic number) which determines the comparative place of an element among its congeners, and
2. The outer electronic grouping which determines an element's valency and hence its group.

The phenomenum of isosterism is directly related to this outer sphere of the atom.

II. Preliminary Work

In 1918, Allen (1,2) suggested from the analogy of molecular weights, that there should be molecular numbers obtained by adding together the atomic numbers of the component atoms in a molecule, in the same manner as the molecular weight is obtained by addition of the atomic weights. He called attention to the fact that the ions of sodium and ammonium, both having a "number" of 11, show a very close kinship in chemical behavior.

III. Langmuir's Original Consideration

Langmuir (3), in 1919, became interested in the structure of carbon monoxide and noted that this compound, though thought to be unsaturated, was a relatively inert substance. Very few other substances combine with it at ordinary room temperatures, which does not fit in with the previously held idea of divalent carbon.

He noted that carbon monoxide resembles nitrogen to an extraordinary extent as is shown by their physical properties, which within the range of experimental error are practically identical.

The evidence shows that carbon monoxide and nitrogen are of nearly identical structural arrangements. The case is amplified by the fact that the total number of electrons in the molecule is the same for both gases.

IV. The Idea of Isosterism

A short time later, Langmuir (4) noted that carbon dioxide and nitrous oxide show the same realtionship that carbon monoxide and nitrogen do. He found that if the cubical models of nitrous oxide and carbon dioxide are built up, they both have the same arrangement, The are identical in electronic grouping, the only difference lying in the nuclear charges of the component atoms.

When the physical properties of these two substances are compared, it is found that they show striking resemblances. Their viscosities, critical temperatures and pressures, densities, and many other properties are practically identical under the same conditions. A difference in freezing points is the only disagreement, and this is explained by the fact that carbon dioxide has a more symmetrical molecule, due to resonance in the nitrous oxide molecule.

	N_2O	CO_2
crit. press. atm.	75	77
crit. temp °K	35.4	31.9
d. at b.p.	0.856	0.856
Sol. in EtOH	3.25	3.13
Heat cond.	0.0506	0.0506
V.p. liqd.	5 atm. (at -6°C)	5 atm. (at -9°C)
F.p.	-102°C	-56°C

When two compounds contain the same number of atoms and the same total number of electrons, they are designated as isosteric compounds or isosteres. Langmuir suggests that isosteres should show remarkable similarities in those properties which do not involve a splitting of the molecule. When molecules are isoelectric (i.e., having the same charge on the comolecules), in addition to being isosteric, this similarity is even closer.

V. Table of Isosteres (4)

isoelectric isosteres nearly identical e.g. $CNO^- + N_3^-$, $CO + N_2$, $CO_2 + N_2O$.

Type	Group, Ion, or Atom
1.	H^-, He, Li^+
2.	$O^=$, F^- Ne, Na^+, Mg^{++}, Al^{+++}
3.	$S^=$, Cl^-, A, K^+, Ca^{++},
4.	Cu^+, Zn^{++}
5.	Br^-, Kr, Rb^+, Sr^{++}
6.	Ag^+, Cd^{++}
7.	I^-, Xe, Cs^+, Ba^{++}
8.	N_2, CO, CN^-
9.	CH_4, NH_4^+
10.	CO_2, N_2O, N_3^-, CNO^-
11.	NO_3^-, $CO_3^=$
12.	NO_2^-, O_3
13.	HF, OH^-
14.	ClO_4^-, $SO_4^=$, $PO_4^{\equiv}$
15.	ClO_3^-, $SO_3^=$, $PO_3^{\equiv}$
16.	SO_3, PO_3^-
17.	$S_2O_6^=$, $P_2O_6^{==}$
18.	$S_2O_7^=$, $P_2O_7^{==}$
19.	SiH_4, PH_4^+
20.	MnO_4^-, $CrO_4^=$
21.	$SeO_4^=$, $AsO_4^{\equiv}$

VI. Prediction of General Properties

No direct comparison can be made of the physical properties of isosteres with different electrical charges. Hence, we would not expect sodium ion to resemble neon, for the electrical force around the sodium ion is sufficient to account for the difference in properties.

It is quite evident, that if two substances resemble each other, then isoelectric isosteres of these two substances resemble each other in physical properties. For example, argon and nitrogen resemble each other quite closely in physical properties. Therefore we will expect the chloride ion (isosteric with argon) and the cyanide ion (isosteric with nitrogen to resemble each other. Many other such relations can be obtained from the table given in Section V.

VII. Crystallographic Applications

By comparison of crystal forms, it is possible to obtain evidence of similarity in arrangement of electrons in isosteric substances even though the charges on the comolecules are different. For example, the sodium and flouride ions are isosteric with the magnesium and oxide ions, so we expect sodium flouride and magnesium oxide to have the same

crystallographic form. This is found to be true. Found also to be of the same form are the compounds magnesium flouride and sodium oxide. Other substances which would be expected to be similar are: potassium chloride and calcium sulfide, potassium sulfide and calcium chloride, cuprous sulfide and zinc chloride, etc.

For a more precise and definite understanding, let us use Barker's rule of isomorphism. Kopp (5) and Retgers (6) regarded substances as isomorphous when they were capable of forming mixed crystals. T. V. Barker, however, maintains that isomorphism should denote similarity of structure.

The following cases of isomorphism are of some consequence:

Type (from table in Section V)	Compounds
2.	NaF, MgO ; MgF_2, Na_2O
3.	KCl, CaS ; $CaCl_2$, K_2S
5.	RbBr, SrSe ; $SrBr_2$, Rb_2Se
7.	CsI, BaTe; BaI_2, Cs_2Te
8.	N_2, CO,
10.	KNCO, KN_3
11.	$NaNO_3$, $CaCO_3$; KNO_3, $SrCO_3$
14.	$KClO_4$, $SrSO_4$, $NaHSO_4$, $CaHPO_4$
15.	$NaClO_3$, $CaSO_3$; $KHSO_3$, $SrHPO_3$
17.	$Na_2S_2O_6$, $Ca_2P_2O_6$
18.	$Na_2S_2O_7$, $Ca_2P_2O_7$
20.	$RbMnO_4$, $BaCrO_4$
21.	$MnSeO_4$, $FeAsO_4$

In all of these cases, the predictions have been verified and the compounds are found to be isomorphous (8).

Quite a few isomorphous compounds exist that seem to bear no relation whatsoever to isosterism. Thus isosterism is not the complete explanation for compounds of this type.

VIII. Specific Studies

Not a lot of verification work has been done on isosteric compounds, but a few works of consequence can be noted as follows:

1. The isosterism of the cyanate and nitride ions

Langmuir (4) made the observation that the ions CNO^- and N_3^- are isosteres, and naturally compounds derived from them are also isosteric. There are very few data available on the physical properties of cyanates and trinitrides, because of the explosive character of the trinitrides and the difficulty of handling them. The salt solubilities and crystal structures (8) are very similar. From this information, it is safe to assume that the salts of cyanic and hydronitric acids will be found to be almost identical.

2. Isosteric Parachors

According to our information, the parachors of isosteres should be equal, if they have the same electrical charge. Copley (9) made many of these parachor measurements and found excellent agreement. He constructs and explains the use of a new parachor chart.

3. Diazomethane and Ketene

Murty (10), in his study of the isosterism between these two compounds, gives support for the open structure of diazomethane. He bases his assumptions on the fact that diazomethane is isosteric with ketene and ketene is a straight molecule.

4. Nitrogen and Carbon Monoxide

Erlenmeyer and Leo (11) review the properties of nitrogen and carbon monoxide. They also give several helpful tables of the isosteres of carbon dioxide and nitrous oxide.

5. Acetylene and Hydrogen Cyanide

Bahr (12) discusses the striking parallel between the properties of acetylene and hydrogen cyanide. He points out that the radical $-C\equiv N$ has properties very similar to the radical $-C\equiv CH$.

$B_2H_6 + C_2H_4$

6. Rotation and Absorption (13)

7. Spectrographic Investigations (14)

8. Organic Compounds (15, 16, 17, 18, 19, 20, 21, 22)

IX. Conclusion

From the above information, it is easy to see that a great deal of investigation of isosteric compounds in relation to physical properties is yet to be carried out. Much information for verification is needed and the phenomenom of isomorphism is wide open for research. One review paper on this subject exists, but it is not available at the present time. The author suggests, when this article becomes available, that it should be excellent reading on this subject. The article will be found in Z. anorg. allgem. Chem., 1942.

See Grimm

Bibliography

1. Stewart and Wilson, "Recent Advances in Physical and Inorganic Chemistry", Longmans, Green and Co., New York, Ed. 7, 1944.

2. Allen, J. Chem. Soc. 113, 389 (1918).

3. Langmuir, J. Am. Chem. Soc. 41, 868 (1919).

4. Langmuir, J. Am. Chem. Soc. 41, 1543 (1919).

5. Kopp, Ber. 12, 868 (1879).

6. Retgers, Z. physik. Chem. 3, 497 (1889).

7. Barker, Trans. Chem. Soc. 101, 2484 (1912).

8. Groth, "Chemische Crystallographie", Leipzig, Pt. I, 1906, Pt. II, 1908.

9. Copley, Chemistry and Industry 59, 675 (1940).

10. Murty, Current Sci. 5 424 (1937).

11. Erlenmeyer and Leo, Helv. Chim. Acta 16, 897 (1933).

12. Bähr, Z. physik. Chem. A168, 363 (1934).

13. Preiswerk, Helv. Phys. Acta 7, 203 (1933).

14. Preiswerk and Erlenmeyer, ibid. 17, 329 (1934).

15. Erlenmeyer and Schmidt, Helv. Chem. Acta 22, 709 (1939).

16. Erlenmeyer and Uberwasser, ibid. 22, 938 (1939).

17. Erlenmeyer and Meyerburg, ibid. 21, 108 (1938).

18. Erlenmeyer and Kleiber, ibid., 111 (1938).

19. Lutz, J. Am. Chem. Soc. 60, 2628 (1938).

20. Erlenmeyer, Kleiber, Loebenstein, Helv. Chem. Acta 21, 1010 (1938).

21. Burger and Bryant, J. Am. Chem. Soc. 63, 1054 (1941).

22. Erlenmeyer, Uberwasser, Weber, Helv. Chem. Acta 21, 709 (1938).

TECHNIQUES IN THE CONSTRUCTION OF LABORATORY APPARATUS

R. A. Penneman April 9, 1946

Many research problems require the construction of apparatus and demand techniques or "know how" which the investigator has not developed. The fact that the same problems have been solved before is often of no help since Chemical Abstracts usually gives no hint of experimental technique. Sources which give leads to specific journal references are given below.

Strong, J., "Procedures in Experimental Physics", Prentice-Hall, New York, 1944

Farkas, A. and H. W. Melville, "Experimental Methods in Gas Reactions", MacMillan and Co., 1939

Müller, R. H., R. L. Garman and M. E. Droz, "Experimental Electronics", Prentice-Hall, New York, 1944

I. GLASS MANIPULATION

A. Breaking Tubing

a. Small tubing (less than 15 mm.)--use wet file mark. Advantages of flat file over more common triangular file.

b. Medium tubing,--file mark and hot glass bead or circular cutters.

c. Large tubing--hot wire or carborundum wheel (such as located in Room 168).

d. For very thin, blown-out tubing, use a diamond scratch.

e. Breakoffsky--use diamond scratch and magnet to move iron. Other techniques.

B. Sealing Operations (1)

a. Polaroid for detection of strain.

b. Strain point is that temperature below which the strain pattern is not altered regardless of cooling rate. A strain will disappear in about 4 minutes at annealing temperature; 4 hours is required at strain point.

Strain Point	Annealing Temp.	Glass
389°C	425°C	Soft
486	521	Nonex
503	570	Pyrex
1020	1120	Quartz

c. Thermal Expansion coefficients (x 10^7)

Lime Glass (G8)	92	Copper	162
Lead Glass (G5)	90	Platinum	91
Nonex (G702P)	36	Tungsten	47
Porcelain (20°-790°)	41	Fernico (25°-450°)	47
Pyrex	32		
Quartz	5.8	Kovar (25°-500°)	56

d. Graded Seals (2). Quartz rod of samll diameter can be sealed directly to pyrex if joint is heated very hot and worked into the quartz.

Soft glass-pyrex seals can be made by grinding glass to powder and mixing in ratio, 4:1, 3:2, 2:3, 1:4 and melting mixes into rods. Rods are applied in a series of rings to join two glasses.

Quartz-pyrex and pyrex-soft glass seals can be purchased; this is recommended since such seals require technique beyond the average chemist's ability.

e. Alundum extraction thimbles can be sealed directly to pyrex tubing to make gas diffusers, etc. (1,4). Large seals should use nonex as an intermediate.

C. Metal to Glass Seals

a. Tungsten wires of less than 1.5 mm diameter can be sealed directly into pyrex. An intermediate of nonex is necessary for diameters up to 4 mm.

The wire is heated to white heat, cleaned of oxides by polishing or heating with $NaNO_2$, washed, and re-oxidized slightly before coating with nonex. A good seal is red. To prevent leaks, end of wire should be sealed with advance or nickel. Copper welds easily to these latter.

b. Platinum wire seals directly to soda or lead glass. Platinum-pyrex seals use the following: Pt, 707, Canary, pyrex. (707 and Canary are special Corning glasses).

Platinum coated glass can be joined by tin or solder to metal wet by these bonding agents. Preparation of these joints described in references (2,3) and involve burning off a platinum compound in presence of organic material to leave an adherent deposit of the metal on the glass.

c. Kovar can be soft soldered, copper-brazed, and spot welded. The coefficient of expansion closely approximates that of Corning G705AJ glass over a wide temperature range above room temp.

Kovar-pyrex seals use the following glasses: Kovar, G705AJ or 705BA, nonex, canary, pyrex. Or, Kovar, G705AJ, 710, nonex, pyrex.

Before sealing, Kovar is heated at about 900°C in wet hydrogen.

d. Copper-pyrex or soft glass seals depend on the use of thin metal at junction so distortion can accomodate difference in expansion coefficients.

e. Iron and steel can be fused to soft glass (3,5) by using flux of equal parts ZnO, borax and powdered soft glass. Metal tube is coated on inside with flux, soft glass; tube to be joined is flared so it meets metal at right angles.

II. BONDING MATERIALS (6)

A. Metallic

a. Properties of Solders

Solder	mp °C	Composition
Woods metal	61	50Bi, 12.5Cd, 25Pb, 12.5Sn
Eutectic	181	36Pb, 50 Sn
Soft solder,	188	50 Pb, 50 Sn
Medium solder	400	20 Ag, 3 Cu, 2 Zn, 75 Sn
Silver solder	720	45 Ag, 30 Cu, 35 Zn
Braxing	875	54 Cu, 46 Zn

A flux for the first four is: 40 $ZnCl_2$, 20 NH_4Cl, 40 H_2O. Dry borax or "Handy Flux" is used for the last two.

Phosphor-bronze alloy (Westinghouse) wets only copper, mp about 750. Excellent for joining parts to copper tubing, can be used Copper to brass with persuasion.

b. Spot welding. (located in Room 168)

c. A laboratory arc welder can be made using a series resistance of about 15 ohms (capable of dissipating 400 watts) and carbon electrodes. An ordinary cone heater will serve as the resistance.

B. Non-metallic (6)

a. Picein, fluid at 80°C, useful adhesive, low v.p.

b. Apiezon compounds. Sealing putty "Q". Apiezon "W"—very low vapor pressure (10^{-3} mm at 180 C), fluid above 80 C. Apiezon "N"--very low vapor pressure stopcock grease.

c. Silver Chloride, mp 455°C, wets most metals and glasses. Used for sealing windows on glass tubes, etc.

d. Irreversible cements; Plaster of Paris; Litharge and glycerol (to 260°C); Water glass and carbonates or oxides of Ca, Mg, Zn, Pb, or Fe; Water Glass and talc forms a cement that holds at red heat; nine parts kaolin and 1 part borax mixed. Water used for ease in application. After evaporation of water, cement is heated slowly to yellow heat to set it.

III. ELECTRICAL DEVICES

A. Miscellaneous

a. Polarized outlets recommended. Laboratory outlets should be marked as to "hot" terminal

b. The 200-C Variac (5 amp) can be operated to give either 0-115, 0-135 volts in clockwise or counter-clockwise rotation. At intermediate voltages, maximum current is 5 amps; at low or high voltages (close to line voltage) 7.5 amps can be drawn.

c. Nickel-chromium alloy wire should not be used in contact with Insa-lute, SauerEisen, or sodium silicate, since the wire is attacked at high temperatures. Alundum refractories are satisfactory. (7)

d. Uses of 12J5, and 117N7 tubes in the laboratory. Advantages of microampere currents through relay points, etc. Circuits given on blackboard.

e. To measure voltages above scale of potentiometer, use two standard cells in series with setting one-half their sum. This doubles range of potentiometer. Alternative method is to connect standard to EMF terminals, set slide wire to one-half standard, and balance. This also doubles range, but requires changing connections at EMF terminals when it is necessary to check the working battery. Both methods put twice normal current through potentiometer.

f. To measure voltages below range of potentiometer use galvanometer and two standard resistors. Circuit given on blackboard.

IV. Miscellaneous Topics

A. To plate Cu on glass dissolve 2 g $CuAc_2$ in 100 ml H_2O, add NH_4OH until ppt dissolves. To 100 ml of this solution add 15 ml 40% hydrazine hydrate. Pour mixed solution in object at 60°C, allow just enough Cu to plate out to make shiny layer. Wash with hot water, place object in water at 60°C and allow to cool slowly to room temperature.

B. Use glacial acetic acid for marking celluloid.

C. Stopcock greases insoluble in organic solvents (9). Mix 25 grams of anhydrous glycerol, 7 grams of dextrin, and 3.5 grams of C.P. d-mannitol. Heat resulting paste to boiling, and allow to cool without stirring. Another type is made by mixing bentonite with glycerol to desired consistency.

D. Devices for delivery of liquids at constant rates. (10)

REFERENCES

(1) Strong, J., "Procedures in Experimental Physics", Prentice-Hall, 1944, Chapter I.

(2) Farkas, A. and H. W. Melville, "Experimental Methods in Gas Reactions", MacMillan and Co., 1939, Chapter V.

(3) McKelvy, E. C. and C. S. Taylor, J. Am. Chem. Soc., 42, 1364 (1920)

(4) Williams, D. and G. S. Haines, Ind. Eng. Chem. (Anal. Ed.) 16, 680 (1944)

(5) Kraus, C.A., United States Patent 1,046,084

(6) Strong J, loc. cit., Chapter 13.

(7) "The Construction of Electrical Furnaces for the Laboratory", Revised Edition, Norton Co., Worcester, Mass.

(8) Jones, J. H., J. Am. Chem. Soc., 64, 965 (1942)

(9) Lange, N. A., "Handbook of Chemistry", Handbook Publishers Inc, Sandusky, Ohio, 1941, p. 1516.

(10) Orchin, M., Ind. Eng. Chem. (Anal. Ed.) 17, 99 (1945)

THE METALLIC BORÖHYDRIDES

Donald Starr April 16, 1946

I. Introduction

The hydrides of boron are a group of compounds which have been of interest for a long time because of their unusual chemical properties and because of their relationship to the ideas of valence and the chemical bond. The simplest compound BH_3 cannot be isolated, although it may have a short existence as an intermediate in certain reactions; it is known as the dimer B_2H_6, a gas which boils at -92°. Others in the series are B_4H_{10}, B_5H_9, B_6H_{10}, and $B_{10}H_{14}$. (9)

The development of the electron theory of valence did not immediately clear up the difficulties in explaining the structures of these compounds. For B_2H_6, for example, it is evident that there are only twelve valence electrons; for the usual ethane-like structure, fourteen are required. This situation produced many suggestions as to the possible structure of the compounds (4). Wiberg suggested that diborane would have the structure of a weak dibasic acid. Sidgwick suggested that two of the hydrogen atoms in diborane were attached through single electron bonds. Another suggestion was that the boron atoms were joined through a resonance bridge of two hydrogen atoms.

Early it was seen that no one proposal for the structure of diborane was in complete agreement with the then known facts. Therefore, much work was done on the chemical properties of the boron hydrides as well as work on their physical characteristics.

II. Borane Salts

One of the very interesting reactions of diborane is its interaction with amalgams of highly active metals (Na, Ca, K) according to equations such as:

$$2M(Hg)_x + B_2H_6 \longrightarrow M_2B_2H_6 + (Hg)_x$$

Stock and his co-workers (10) prepared a number of borane salts from B_2H_6, B_4H_{10}, and B_5H_9. The non-volatile white solids produced were quite stable; the addition of two electrons to the electronically unsaturated diborane would lead to an ion having a structure analogous to that of ethane, and therefore stability would be expected.

III. Prediction of Metal BH_4 Compounds

It had long been postulated that compounds with the anion (BH_4^-) should exist. It may be presumed (4) that B, C and N^+ have identical electronic configurations in the ground state; from this it should follow that (BH_4^-) should exist since CH_4 and NH_4^+ are known.

Stock and Laudenklos (11) were unsuccessful in their attempts to prepare KBH_4 by the action of atomic hydrogen on potassium diborane, $K_2B_2H_6$. Thomas and Stevens (12) reported that they failed to prepare salts of the type $M(BR_4)$, where R is a hydrocarbon radical, by heating trimethyl boron with ethyllithium, lithiumphenyl, and other metal alkyls.

IV Preparation of the Borohydrides

Schlesinger, Sanderson, and Burg (7) reported that they obtained a new compound of aluminum, boron, and hydrogen by treating trimethyl aluminum with an excess of diborane. The volatile compound was determined by analysis and molecular weight checks to be AlB_3H_{12} and was termed aluminum borohydride. "Borane salts" were used for those compounds formed by the addition of metals to the boranes, whereas other salts containing the same constituents, but in different proportions, were called "metallic borohydrides". Reports on other metal-boron-hydrogen compounds followed this first preliminary observation. (8, 2, 5, 6)

A. Aluminum Borohydride

$$Al_2(CH_3)_6 + 4B_2H_6 \longrightarrow 2B(CH_3)_3 + 2AlB_3H_{12}$$

For a satisfactory preparation the diborane must be present in a quantity somewhat greater than indicated by the equation. The physical properties of the compound are those of a non-polar substance. Its chemical properties resemble those of diborane greatly; its reactions with air, water, HCl are analogous to those of diborane.

B. Beryllium Borohydride

The similarity between beryllium and aluminum suggested that diborane might react with dimethyl beryllium to give beryllium borohydride. The reaction went and in steps that could be recognized, and intermediate products were isolated. (2)

$$Be(CH_3)_2 \; x \xrightarrow{B_2H_6} (CH_3)\,BeBH_4 \xrightarrow{B_2H_6} HBeBH_4 \xrightarrow{B_2H_6}$$

$$(BH_4)\,Be(BH_4)$$

Burg and Schlesinger intended the above series to represent the series of reactions; they did not propose this as a mechanism or suggestion of structure.

The final product of the reaction, BeB_2H_8, showed many properties that closely related aluminum borohydride with it. Its reactions with air, water, and HCl are similar. In physical properties it differs more decidedly from the aluminum compound. Although both are readily vaporized at room temperature, the beryllium compound is less volatile than the aluminum borohydride, and its melting point is about 180° higher. These differences indicate that the beryllium borohydride may be more polar in character.

C. Dimethyl Gallium Borohydride

At -45° in a typical experiment trimethylgallium was treated with an excess of diborane (5) and the crystalline borohydride formed was found to melt at 1.5°. This was reported in a preliminary observation and is being investigated further.

D. Lithium Borohydride

$$2C_2H_5Li + 2B_2H_6 \longrightarrow 2LiBH_4 + (C_2H_5)_2B_3H_4$$

The reactions of the methyl derivative of aluminum and beryllium lead Schlesinger and Brown to try to prepare a similar derivative of an alkali metal. (5) A very stable solid, $LiBH_4$, is produced according to the above equation. This compound reacts with HCl and H_2O similarly to its analogs. However, lithium borohydride differs in a number of respects from the aluminum and beryllium derivatives. Lithium borohydride is unaffected by dry air. Its salt-like character (m.p. 275 with decomposition and no appreciable vapor pressure up to this point) is another striking difference. While trimethylamine removes borine groups from the Al and Be derivatives (the latter with a little more difficulty), it has no effect on $LiBH_4$. Another way to prepare $LiBH_4$ is as follows:

$$Al(BH_4)_3 + 3LiC_2H_5 \longrightarrow 3LiBH_4 + Al(C_2H_5)_3$$

This should indicate that the basic structures of the aluminum and lithium borohydrides are closely related. An example of the long predicted class of compounds, $M(BH_4)$, was prepared by the reaction of trimethyl boron with ethyllithium.(5) Schlesinger and Brown seemed to have no doubt that this was an example of a quaternary boron derivative $Li\ C_2H_5B(CH_3)_3$. Recently, the commercial availability of lithium borohydride was announced. (13)

V. Comparison of Chemical and Physical Properties (5)

	Diborane	Aluminum Borohydride	Beryllium Borohydride	Lithium Borohydride
Anal. formula	B_2H_6	AlB_3H_{12}	BeB_2H_5	$LiBH_4$
Reaction formula	$(H_3B)_2$	$Al(BH_4)_3$	$Be(BH_4)_2$	$LiBH_4$
M.p. °C.	-165.5	-64.5	123°	+275°
B.p. °C.	-92.5	44.5	91.3°	dec. 275°
V.p. at 0°, mm	very high (415.000)	119	0.5	very low ($\ll 10^{-5}$

Increasing tendency to react as BH_4 derivatives →

← Increasing tendency to react as BH_3 derivatives

The data in the table indicate that there is a transition from diborane to lithium borohydride. The latter appears to be rather polar in character while the former is decidedly non-polar in nature. It seems that in some respects, the Al compound is more like diborane and the Be compound is more like lithium borohydride. Similar relationships exist in the chemical behavior. There appears to be a trend in the reaction with trimethylamine.

Schlesinger (5) suggested that $LiBH_4$ consisted of Li^+ and BH_4^-; then assuming an analogous structure for the Al or Be compound, it is seen that the smaller and more highly charged Al and Be ions would exert a much greater deforming influence on the BH_4^- ion. As a result, the polar character of the Be compound would become less than that of the Li borohydride and still less in the Al compound, as is actually the case. The deformation of the BH_4^- would make it more susceptible to disruption.

VI. Structure Considerations

The configuration of aluminum borohydride has been determined by Beach and Bauer (1) using electron diffraction methods. They propose the $Al(BH_4)_3$ structure where there are several resonance hybrids possible. No experimental work

has been done on lithium or beryllium borhydride; but the ionic structure for lithium borohydride does not seem improbable, and for beryllium borohydride these investigators suggest $Be(BH_4)_2$ by comparison with $Al(BH_4)_3$.

Longuet-Higgins and Bell (3) have suggested certain bridge link d structures for the more volatile borohydrides. They also believe $LiBH_4$ to be ionic.

VII. BIBLIOGRAPHY

(1) Beach and Bauer, J. Am. Chem. Soc. 62 3440 (1940)

(2) Burg and Schlesinger, ibid. 62 3425 (1940)

(3) Longuet-Higgins and Bell, J. Chem. Soc. 1943 252

(4) Palmer, W. G.: "Valency - Classical and Modern", pp. 60, 133, 225. Cambridge University Press, Cambridge (1944)

(5) Schlesinger and Brown, J. Am. Chem. Soc. 62 3429 (1940)

(6) Schlesinger, Brown, and Schaeffer, ibid. 65 1838 (1943)

(7) Schlesinger, Sanderson and Burg, ibid. 61 536 (1939)

(8) Schlesinger, Sanderson and Burg, ibid. 62 3421 (1940)

(9) Stock, A., "Hydrides of Boron and Silicon", Cornell University Press, Ithaca, N. Y. (1933)

(10) Stock, A., Z. anorg. Chem. 225 225 (1935)

(11) Stock and Laudenklos, ibid. 228 178 (1936)

(12) Thomas and Stevens, J. Chem. Soc. 1933 556

(13) Chem. and Eng. News 24 680, 1946

MAGNESIUM METAL PRODUCTION

Henry Holtzclaw April 28, 1946

A. Introduction

Magnesium is a silvery-white, malleable, ductile metal which weighs 109 pounds per cubic foot. It is the eighth most abundant element and the sisth most abundant metal. It can be cast, extruded, rolled, welded, and machined and forms alloys of great strength with Zinc, aluminum, and manganese. The average amount of magnesium used in each plane during World War II was nearly one-half ton (13). Whereas production was 122 tons in 1925, 20,500 pounds were produced in only one month during the first quarter of 1944 (19). The price has dropped from $5 per pound in 1914 to 20.5 cents per pound in 1943 (4).

B. History

Sir Humphrey Davy, in 1808, discovered the element magnesium when he found it as one component of Epsom salt ($MgSO_4$). (6, 15). In 1830, Bussy obtained the first pure magnesium metal, and Bunsen obtained the metal by electrolysis of fused magnesium chloride in 1852. German industry began using Bunsen's process in 1886. The United States bought all of its magnesium from Germany until 1914, when the supply was shut off and the price rose to $5 per pound. Dow Chemical Company and American Magnesium Corporation (6,15,19) became the principal United States producers. In 1927, American Magnesium Corporation became a fabricator only, thereby giving Dow a monopoly which it held until 1941 (6,19). Dow began sales to foreign countries (6) in 1928, sales being made principally to England, Poland, Holland, Mexico, Japan, and Germany. Export sales became the major portion of total sales during the 1930's. Great Britain began producing in 1935, when Magnesium Elektron Ltd., was founded. The company used the process of I. G. Farbenindustrie of Germany, largest manufacturer of magnesium in Europe.

C. Production for World War II

I. Production in United States--Between 1939 and 1943, fourteen plants were built in the United States with both government and private funds (19). Plants were owned by the government and managed by the various companies.

TABLE (19)

a. Electrolytic Processes

1. Dow Chemical Company:

(a) From brine--Magnesium extracted in Midland, Michigan comes from a fossil sea that lies under the state. (5) Brine containing 3.5% magnesium chloride is pumped to the plant where it is dried, first in air and then in hydrogen chloride atmosphere, and electrolyzed, producing magnesium metal and chlorine gas (6). 99.9% pure magnesium is obtained (15,14).

Rated Annual Production Capacity of Mg Plants in U. S.

Ownership and Operating Company	Location	Process	Rated Capacity in million lbs.	Approximate Gov't Investments (in units of $1000)
Privately Owned:				
Dow Chemical Company	Midland, Mich.	Electrolytic	18	
Dow Chemical Company	Freeport, Tex.	Electrolytic	18	
Permanente Metals Corp.	Permanente, Calif.	Carbothermic	24	
Total Privately Owned	- - - - -	- - - -	60	
Government Owned:				
Dow Chemical Company	Freeport, Tex.	Electrolytic	18	8,200
Dow Magnesium Company	Velasco, Tex.	Electrolytic	72	55,100
Dow Magnesium Company	Marysville, Mich.	Electrolytic	72	38,400
International Minerals and Chemical Company	Austin, Tex.	Electrolytic	24	18,400
Diamond Magnesium Company	Painesville, Ohio	Electrolytic	36	14,300
Basic Magnesium, Inc.	LasVegas, Nev.	Electrolytic	112	130,000
Mathieson Alkali Works, Inc.	Lake Charles, La.	Electrolytic	54	48,500
New England Lime Company	Canaan, Conn.	Ferrosilicon	10	4,300
Magnesium Reduction Company	Luckey, Ohio	Ferrosilicon	10	4,700
Electro Metallurgical Co.,	Spokane, Wash.	Ferrosilicon	48	16,100
Ford Motor Company	Dearborn, Mich.	Ferrosilicon	40	10,400
Amco Magnesium Corp.	Wingdale, New York	Ferrosilicon	10	7,000
Permanente Metals, Corp.	Manteca, Calif.	Ferrosilicon	20	6,200
Total Government Owned	- - - - - -		526	
Grand Total	- - - - - - -		586	

Compiled by U. S. Tariff Commission

(b) From sea-water--Dow Chemical Co., in 1943, opened a plant in Freeport, Texas, for production of magnesium from sea-water (12, 15, 9). Lime, made from oyster shells, is reacted with the sea-water to make magnesium hydroxide, which is filtered off and reacted with hydrochloric acid. The resulting magnesium chloride is partially dried and used as cell feed for Dow electrolytic cells. Chlorine obtained in the electrolysis is recycled to produce hydrochloric acid (15):

$$CH_4 + H_2O \longrightarrow 3H_2 + CO_2$$

$$H_2 + Cl_2 \longrightarrow 2HCl$$

The Freeport plant also extracts bromine from the sea for manufacture of ethylene dibromide for high octance gasoline. Forty-two other materials could be removed from the waste sea-water, but processes are not commercially feasible as yet.

Diamond Magnesium Co.--The plant, located at Painesville, Ohio, utilizes Dow electrolytic cells, but the preliminary method of obtaining magnesium chloride differs from Dow's method (1). The plant is coordinated with a near-by ammonia-soda plant. By product, chlorine, is converted to calcium hypochlorite, 120 tons being produced per day during the war:

$$2\ Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + H_2O$$

$$2\ NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$

$$CaCl_2 + 2NaOCl \longrightarrow Ca(OCl)_2 + 2NaCl$$

2. Basic Magnesium, Inc., Les Vegas, Nevada, uses a process developed under supervision of Magnesium Elektron, Ltd. (2) originated by I. G. Farbenindustrie of Germany:

$$MgO + CO + Cl_2 \longrightarrow MgCl_2 + CO_2$$

The molten, anhydrous magnesium chloride is used as feed for electrolysis.

3. Miscellaneous--International Mineral and Chemicals uses Dow Electrolytic cells to electrolyze magnesium chloride (12). The Mathieson Alkali Works and the Consolidated Mining and Smelting Co. of Canada use an electrolysis method developed jointly by them (12).

b. Ferrosilicon Process (Pidgeon)--Ford Motor Co. reduces calcined dolomite with crushed 75% ferrosilicon (12) at 2100 degrees Fahrenheit. Magnesium is liberated as a vapor and deposited on an air-cooled condenser.

c. Carbothermic Process (Hansgirg)--Permanente Metals Co., Permanente, Calif., use a process by which magnesium oxide (12) obtained by treatment of dolomite, is reduced by carbon at high temperature. The magnesium vapor is shock-cooled by natural gas (16). A by-product, magnesium black, consisting of a mixture of carbon magnesium oxide and magnesium dust (19), is sold to synthetic rubber, refractory, and rayon industries.

II. Production in Other Countries--In 1943, Germany produced magnesium at the rate of 100,000,000 pounds per year, Japan at the rate of 28,000,000 pounds per year, and Great Britain at the rate of 72,000,000 pounds per year (13).

1. Production in Great Britain--Four companies produce magnesium metal (3), of which the only one in active production is Magnesium Elektron Ltd. (2, 10). The other plants which never progressed past pilot plant stage, used a thermal ditillation with ferro-silicon reducing agent, a carbothermic process, and a thermal process with calcium carbide as reducing agent.

2. Miscellaneous--Thermal reduction and ferro-silicon processes have been used in Canada. Carbide reduction has been used in Canada. Carbide reduction has been used in Australia (13).

D. Research for New Processes

Following are three examples of research processes which have received patents but have never been utilized commercially.

H. H. Dow and E. O. Barstow (17) obtained patents, in 1930, for:

$$MgCO_3 \cdot CaCO_3 + SO_2 \longrightarrow MgCl_2 + CaSO_4 + 2CO_2$$

The calcium sulfate is filtered out leaving magnesium chloride in solution, which is then evaporated to dryness. Chlorine obtained from later electrolysis makes possible a cyclic process. Satisfactory raw materials, however, are expensive and the by-products are so cheap that they do not aid materially in bringing down cost of process, causing the method to be of small promise commercially.

H. S. Booth obtained a patent (17) in 1938 for preparation of magnesium oxide by dissolving dolomite in fused sodium chloride or potassium chloride and effecting a separation of the magnesium carbonate and calcium carbonate by maintaining a temperature between the two decomposition temperatures. The magnesium carbonate decomposes, forming a precipitate which may be filtered out. The calcium carbonate remains in solution. The process is of doubtful success, commercially, because of the expensive solvent and several difficult and costly steps.

A proposed process for obtaining magnesium hydroxide, worked out and patented by J. D. Delang (17) in 1919 might have commercial possibilities in areas with low cost electric power:

$$CaCO_3 \cdot MgCO_3 + MgSO_4 + 6H_2O \longrightarrow 2\,Mg(OH)_2 + 2H_2 \text{ (all at cathode)}$$
$$+ CaSO_4 \cdot 2H_2O + 2CO_2 + O_2 \text{ (all at anode).}$$

The magnesium sulfate may be obtained from a reaction of dolomite and niter cake (by-product in manufacture of nitric acid from sulfuric acid and sodium nitrate). The hydrogen and oxygen obtained would have market value.

E. Predictions for Future of Magnesium Metal

As early as July, 1944, the United States Government closed five of the fourteen plants recently built, and limited the production of four others. By the end of 1944, production was completely stopped in all but four government-owned plants (19). The U. S. Tariff Commission, after a thorough investigation of magnesium industry during the early part of 1945, estimated (18) post-war consumption of magnesium to be 64.5 million pounds, as compared to a total production capacity of between 500 and 600 million pounds. 40.5 million pounds would be utilized by the transportation industry. Some active work is being carried on to encourage the magnesium industry in western United States to continue production (8). The situation, in general, is not too promising for selling govenrment plants to private concerns (19). The U. S. Tariff Commission feels that the Dow process and the Permanente carbothermic process are most likely to succeed in post-war years and will be able, jointly, to produce more than the total consumption. The only hope of new entrants to the field, therefore, would be in the event of increased consumption, or ability to produce the magnesium appreciably cheaper than either Dow or Permanente. Some plants may be changed over to other products. The Mead, Washington ferrosilicon magnesium plant operated by Electro Metallurgical Co., for example, is now producing metallic sodium (7).

New improvements in fabrication of the metal allow many applications which before the war were considered impractical. Decreased cost of production of magnesium should take place, which would encourage further use, but Arthur Lowery predicts (11) on the basis of his experience with the War Production Board, that the price cannot go lower than about fifteen to sixteen cents per pound.

BIBLIOGRAPHY

1. Avery, J. M., and Evans, R. F., Chem. and Met. Eng., 52, 94 and 130 (April, 1945)

2. Ball, C. J. P., Metallurgia, 32, 153 (Aug., 1945)

3. Butterbaugh, H. W. Atkins, T. W., and Davidson, L. H., Modern Metals, 1, 8 (Aug., 1945)

4. Cone, E. F., Metals and Alloys, 17, 692 (March, 1943)

5. Doan, L. I., Ibid, 18, 547 (Sept., 1943)

6. Dow, W. H., Metal Progress, 45, 675 (April, 1944)

7. Editor, Chem. and Met. Eng., 52, 168 (Sept., 1945)

8. Grant, L. B., Ibid, 52, 262 Nov., 1945)

9. Kirkpatrick, S. D., Chem. and Met. Eng., 48, Special section at beginning of issue, (Nov., 1941)

10. Knight, H. A., Metals and Alloys, 17, 57 (Jan., 1943)

11. Lowery, A., Technology Review, 47, 236 (Feb., 1945)

12. Manning, P. D. V., Metals and Alloys, 18, 547 (Sept., 1943)

13. Metallurgia, 29, 79 (Dec., 1943)

14. Metal Progress, 48, 497, (Sept., 1945)

15. Stedman, G. E., Metals and Alloys, 20, 941 (Oct., 1944)

16. Stedman, G. E., Ibid, 22, 102 (july, 1945)

17. U. S. Bureau of Mines, Inf. Circ. No. 7247 (Aug. 1943)
    Includes following patents used:
    Booth, H. S., U. S. Patent 2,112,904 (April, 1938)
    Delange, J. C., Brit. Patent 134,626 (Nov., 1919)
    Dow, H. H., and Barstow, E. O., U. S. Patents 1,749,210 and 1,749,211 (March, 1930)

18. U. S. Tariff Commission, Chem. and Met. Eng., 52, 80 (April, 1945)

19. U. S. Tariff Commission, Ibid, 52, 133 (May, 1945)

PHOTOCONDUCTIVITY IN ALKALI METAL HALIDES

C. J. Nyman April 30, 1946

Introduction

The photochemical properties of the alkali metal halides have been investigated largely by Hilsch and Pohl (7), Mott and Gurney (3,4,5,6), de Boer (1), and their co-workers. It has been found that these crystals under ordinary conditions are insulators, and do not conduct a current on illumination with light. However, when an excess of alkali metal atoms is added to the crystal, illumination with the proper wave lengths of light will cause the liberation of photoelectrons within the crystal. The absorption spectra (F-band) of such a crystal with dispersed alkali metal atoms is considerably different from that of the pure crystal. The illumination of the crystal containing alkali metal atoms with wave lengths of light in its F-band gives rise to a third type of spectra (F'-band) when an electric field is applied to the crystal. By illumination of this crystal with light in its F'-band, a change occurs which causes the reappearance of the original F-band. In both of these latter two transitions, the production of photoelectrons is observed by placing the crystal between two electrodes in series with a galvanometer or electrometer and applying a high potential to the electrodes.

Absorption Spectra Of Pure Alkali Halides.

Hilsch and Pohl (7) found that the alkali halides have absorption bands in the ultraviolet ranging from 0.1 to 0.24 microns, and that the position of the principal maximum nearest the visible is determined essentially by the halide ion. The effect of the alkali ion seems to be of secondary importance. The position of the maximum moves toward the longer wave lengths as the atomic weight of the halogen increases. This maximum corresponds to the amount of energy necessary to convert a halide ion into a halogen atom in the normal state within the lattice.

Mott and Gurney (5,6) consider that the electron is free to move throughout the crystal until it becomes lodged in a hole in the crystal at the center of six alkali ions. They consider that even a nearly perfect optical crystal contains vacant lattice points, the number of positive ions missing being equal to the number of negative ions missing.

Hilsch and Pohl (7) and others (1,2,8) consider that the electron moves from the halide ion to one of the six nearest alkali metal ions, forming a neutral halogen atom and an alkali metal atom.

Production of F-Centers. (1,5,7).

The transfer of an electron by either of the two methods above gives rise to a new absorption band called the F-band which lies in the region of 0.5 microns. The absorption centers involved are called F-centers, "Farbzentren", or Color centers.

F-centers with identical properties may be produced by heating the alkali halide crystal in a vapor of the alkali metal at high temperatures and suddenly quenching. The number of F-centers produced per cc is proportional to the number of alkali metal atoms per cc of vapor surrounding the crystal.

F-centers may also be produced by irradiation with X-rays in much the same fashion as with ultraviolet light. In any case, there is a limit to the number of F-centers produced, depending on the number of defects in the crystal.

Photoconductivity

Pohl (7) defines the primary photoelectric current as that which flows when the electrons of an insulator are raised to the conduction levels by illumination in its absorption band. In some crystals, the continued passage of a primary current appears to break down the resistance of the crystal, and allows electrons to enter the conduction levels from the cathode. Such a current is a secondary photoelectric current. The primary current is proportional to the distance the electron moves toward the anode (range of the electron), and the number of F-centers per cc of the crystal. As the field strength increases, a saturation value is quickly attained.

When F-centers are illuminated with light in their absorption band, photoelectrons are emitted. These electrons move through the lattice until they are either trapped in another vacant lattice point similar to the one they were ejected from, or until they are trapped by another F-center. Two electrons are now trapped in a single hole, and give rise to a new absorption band further toward the red at about 0.7 microns. This new band is called the F'-band and the centers with two trapped electrons are called F'-centers. When the F'-centers are illuminated with light of their absorption band, the second electron is emitted, and two F-centers are reformed. This explanation agrees with the experimental observation that for every F'-center formed, two F-centers are destroyed.

To describe the mechanism of the photoelectric current, consider first a crystal containing a certain number of F-centers, but with no applied field. An electron released by the light will execute a type of Brownian path until it is captured by an F-center. The length of the Brownian path is naturally inversely proportional to the number of F-centers per cc. When a field is applied to the crystal, the mean distance that an electron drifts down the field is directly proportional to the total length of the Brownian path, and inversely proportional to the number of F-centers per cc. At low temperatures, this

current can be measured and is found to start and stop instantaneously with interrupted illumination. At higher temperatures, a dark current is observed. The primary photoelectric current is proportional to the field applied at low potential gradients, but reaches a saturation value very rapidly as the gradient is increased above 200v/mm.

The Migration of F-Centers.

If a crystal containing a stoichiometric excess of alkali metal is mounted between two electrodes in a field greater than 200v/cm and at temperatures above 300°C., the color is observed to migrate toward the anode. The electrons are ejected from their holes and move toward the anode, and the vacant lattice points appear to move toward the cathode. At these temperatures, the crystal is an electrolytic conductor, and the electrons will form new color centers on drifting into previously uncolored regions.

BIBLIOGRAPHY

1. de Boer, J. H.; "Electron Emission and Adsorption Phenomena", Cambridge (1935).
2. Klemm, W.; Z Physik, 82, 529, (1933).
3. Gurney, R. W. and Mott, N. F.; Trans. Faraday Soc.; 34 506, (1938).
4. Mott, N. F.; Trans. Faraday Soc; 34, 500, (1938).
5. Mott, N. F.; and Gurney, R. W.; "Electronic Processes in Ionic Crystals", Oxford, (1940).
6. Mott, N. F. and Littleton, N. J.; Trans Faraday Soc., 34, 485, (1938).
7. Pohl, R. W. (and Hilsch, R.); Proc. Phys. Soc.; 49, 3, (1937)*.
8. Von Hippel, A; Z Physik, 101, 680, (1936).

* Review of work by Pohl, Hilsch, and co-workers.

DONOR PROPERTIES OF PHOSPHORUS AND SULPHUR COMPOUNDS

Clayton Callis May 7, 1946

Tricovalent phosphorus compounds, like ammonia and its derivatives, and dicovalent sulfur compounds, like water and its derivatives, would be expected to be capable of complex formation by coordination through an unshared pair of electrons. However, H_2O and H_2S show very little similarity in their coordinating tendencies; the same is true for NH_3 and PH_3.

The difference between H_2O and H_2S is indicated by their dissimilarity as solvents, H_2S being very poor in this respect; and also by the marked difference in the stability of their coordination compounds. (1) (2) Considerable work has been done on the thiohydrates by Biltz and Keunecke. (1)

The series of coordination compounds with nitrogen and with phosphorus have very little in common. Nearly all the known complexes of phosphorus are non-ionic and are of several types which are very characteristic. After examining the experimental evidence, it might well be concluded that these compounds exist solely because of the additional stability of a configuration made possible by the addition of a phosphine or substituted phosphine molecule.

Since the phosphine molecule possesses a lower dipole moment than the ammonia molecule (4) its donor ability would be expected to be much smaller than that of ammonia. The substitution of larger groups, whether positive or negative, in general, appears to increase this ability; for coordination compounds of the trialkyl phosphine and phosphorus trihalides are comparable to those of ammonia. It is interesting to note that this is not generally true in the case of ammonia and its derivatives except in the simplest case, i.e., in their coordination compounds with the hydrogen ion. Perhaps this can be explained by a consideration of steric hindrance since the N has an atomic radius of 0.53 and P 1.08 A.

The linkage of the metal to a substituted phosphine is very firm and the substituted phosphine group is not easily displaced. In many cases the phosphine appears to be held more firmly than halogens or other charged groups.

On more or less theoretical grounds, several investigators, especially Holtje (4), who carried out rather extensive experiments with the group IV halides, have suggested that the compounds of PH_3 and H_2S should bear close resemblance to each other just as the compounds of ammonia are akin to those of water.

The following table gives a summary of the data compiled by Holtje (4) concerning the coordination compounds of PH_3 with the group IV halides. For convenient comparison the table also contains results of the behavior of the salts toward H_2S and NH_3.

Salt	M.P.	PH_3(4)	Behavior toward H_2S (1)	NH_3
CCl_4	-23.8	s. in liq. PH_3	s. in liq. H_2S	-----
$SiCl_4$	-68.7	s. in liq. PH_3	s. in liq. H_2S	converted to $Si(NH_2)_4$
$GeCl_4$	-49.5	s. in liq. PH_3	----------	converted to $Ge(NH)_2$
$SnCl_4$	-33	2 $SnCl_4 \cdot 3PH_3$ (yellow)	$SnCl_4 \cdot 2H_2S$ $SnCl_4 \cdot 4H_2S$ (white)	$SnCl_4 \cdot 2NH_3$ $SnCl_4 \cdot 4NH_3$
SnI_4	+145	no reaction	no reaction	several ammoniates
$PbCl_2$	-15	reduced to $PbCl_2$	reduced to $PbCl_2$	several ammoniates
$TiCl_4$	-24	$TiCl_4 \cdot PH_3$ $TiCl_4 \cdot 2PH_3$ (yellow)	$TiCl_4 \cdot H_2S$ $TiCl_4 \cdot 2H_2S$ (yellow)	several ammoniates
$ZrCl_4$	-----	no reaction	no reaction	several ammoniates
$AlCl_3$	+190	no reaction	$AlCl_3.H_2S$	several ammoniates
TiI_4	+150	no reaction	no reaction	-------
GeI_4	+144	no reaction		

Observations and generalizations made by Holtje on this rather small amount of information:

1. Salts behave similarly toward PH_3 and H_2S.
2. Biltz and Keunecke concluded that only salts with molecular lattices (low melting) react with H_2S. Holtje asserts the same is true for PH_3.
3. The reaction with PH_3 shows the similarity between Ge and Si.
4. PH_3 possesses scarcely any similarity to NH_3 in these reactions.
5. PH_3 and NH_3 are in similar relation to each other as H_2S and H_2O.
6. The similarity in the coordinating tendencies of PH_3 and H_2S parallels that of NH_3 and H_2O.

The phosphine compounds are considerably more stable than the sulphines or thiohydrates. The decomposition pressures of the thio-ethers are (around 0°C) generally greater than 100 mm., while with the phosphines, the decomposition pressures are only a few mm (4). Stability has been evaluated from decomposition pressures, temperature-pressure curves, and calorimetric determinations of the heats of reaction. (11)

The greater stability of the phosphine compounds can not be explained on the basis of dipole moment; for H_2S has a higher dipole moment than phosphine.

	U	R (Molecular Refraction)
NH_3	1.50	5.60
H_2S	0.931	9.45
PH_3	0.55	11.73

If one considers also the deformability of the donor molecule the stable compounds of PH_3 seem plausible (6).

The negative constituent of the salt also influences the stability of the compound; the chlorine containing compounds being less stable than those containing bromine.

Since the stability of the phosphine and sulphine compounds is greatly increased by substitution, there is a greater opportunity for comparison among the coordination compounds of the dialkyl sulfines and the trialkyl phosphines.

CLASSIFICATION

Except for a few minor exceptions, all of the known addition compounds of phosphorus are of the simple additive type

$$a\ M^m\ X_m \cdot\ bPR_3$$

where M represents a metal of valence m, X is a univalent radical, R may be hydrogen, a halide, or an alkyl or alkyloxy group. In the table nothing is implied as to structure.

	a:b = 2:1	a:b = 3:2	a:b = 1:1	a:b = 2:3	a:b = 1:2
Cu^{+1}			CuX,PR_3		$CuX\cdot 2PR_3$
Ag^{+1}	$2AgX.PR_3$		$AgX\cdot PR_3$		
Au^{+1}			$AuX\cdot PR_3$		
Cd^{+2}			$CdX_2\cdot PR_3$	$2CdX_2\cdot 3PR_3$	$CdX_2\cdot 2PR_3$
Hg^{+2}	$2HgX_2.PR_3$	$3HgX_2.2PR_3$	$HgX_2\cdot PR_3$	$2HgX_2\cdot 3PR_3$	$HgX_2\cdot 2PR_3$
Pd^{+2}			$PdX_2\cdot PR_3$		$PdX_2\cdot 2PR_3$
Pt^{+2}			$PtX_2\cdot PR_3$		$PtX_2\cdot 2PR_3$
Au^{+3}			$AuX_3\cdot PR_3$		
B^{+3}	$2BX_3.PR_3$		$BX_3\cdot PR_3$		
Al^{+3}			$AlX_3\cdot PR_3$		
As^{+3}			$AsX_3\cdot PR_3$		
Sb^{+3}	$2SbX_3.PR_3$				
Bi^{+3}			$BiX_3\cdot PR_3$		
Ti^{+4}			$TiX_4\cdot PR_3$		$TiX_4.2PR_3$
Sn^{+4}				$2SnX_4\cdot 3PR_3$	

The number of known coordination compounds of H_2S is indeed very small. The more important ones are (1);
$AlCl_3\cdot H_2S$; $AlBR_3\cdot H_2S$; $AlI_3\cdot 2H_2S$; $AlI_3\cdot 4H_2S$;
$BeBr_2\cdot 2H_2S$; $BeI_2\cdot 2H_2S$; $TiCl_4\cdot H_2S$; $TiCl_4\cdot 2H_2S$;
$TiBr_4\cdot H_2S$; $TiBr_4\cdot 2H_2S$; $SnCl_4\cdot 2H_2S$; $SnCl_4\cdot 4H_2S$.

Several sulphines of the type $[MX_2 \leftarrow SR_2]$, particularly of platinum, palladium and mercury have been investigated (7), (8), (9), (10), (41).

NOMENCLATURE

All the compounds of known structure can be named according to the accepted system. For uniformity, it is perhaps best to consider the phosphorus halides and the esters of phosphorous acid as derivatives of phosphine. In a like manner, the compounds of H_2S are named as substituted sulfines.

STRUCTURE

There is very little evidence on the structure of many of these compounds. The type of work that has been done is indicated below.

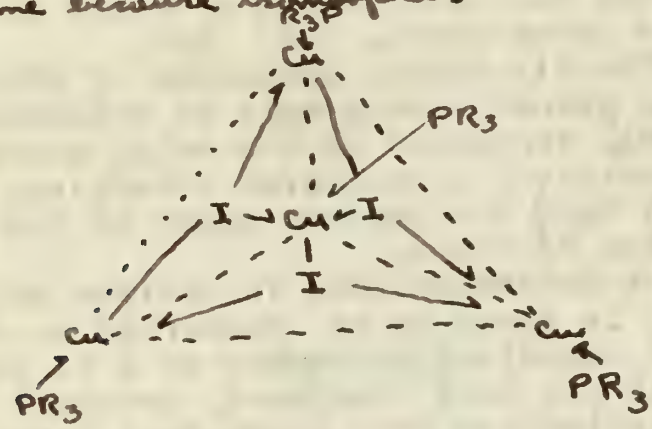
A. X-ray studies
   1. The structure of $[R_3P \dashrightarrow MX]$, where M is Ag or Cu, has been thoroughly investigated. The molecule is four-fold with the metal atoms arranged at the corners of a regular tetrahedron. (15) (19).
   2. A study of the disulphine compounds of platinum supports the planar arrangement of valencies (17).
   3. $[(Hg,Cd)X_2 \cdot PR_3]$ compounds in the solid state have the dimeric symmetrical tetrahedral structure. (12)
   4. In $[2PR_3 2PdCl\ C_2O_4]$ the oxalato group is the bridge connecting the Pd atoms.
B. Molecular weight determinations in various solvents. Between 3 & 4.
   1. $[H_3P \rightarrow CuI]$ is shown to be four-fold in solution (15).
   2. Gold shows a coordination number of 2 in compounds of the type $[R_3P \dashrightarrow AuCl]$ (solvent, benzene) (19)
   3. Several investigators have shown that formulas of the compounds of the type $[PtCl_2 \cdot R_2S]$ and $[PtCl_2 \cdot PR_3]$ should be doubled (18) (25) (26).
   4. The unimolecular formula $[2R_3P \dashrightarrow MX_2]$ was found to be correct for Hg, Pt, Pd, and Cd. (12). cis & trans incl. for Pt
C. Chemical Evidence
   1. Study of α-α' dipyridyl derivatives (15).
   2. Structure and isomerism of phosphine and sulphine compounds of platinum and palladium compounds (20) (9) (21) (10) (28).
   3. Studies of solubilities in various solvents with analogies to known compounds.
D. Dipole moment measurements
   1. Existence of trans isomers in the platinum and palladium compounds is verified (22).
E. Crystallographic studies
   1. Mann, Purdie and Wells have confirmed the unimolecular formulas of the aurous compounds $[AuCl \leftarrow PR_3]$ (19).
   2. Study of Cs_2,Au_2Cl_6 crystals confirms linear and planar configurations of gold. (42).

OTHER WORK DONE IN ESTABLISHING EMPIRICAL FORMULAS

A. Observations of the volume ratios of the gas generated in dissociation (29).
B. Conductivity measurements. Jensen (18) worked with the conductivity of aqueous solutions of B-$[PtCl_2 \cdot (Et_2S)_2]$.
C. Vapor pressure curves used to calculate calorific data

A

1. X-ray diffr. of $[CuX \cdot AsR_3]$ show $[CuX \cdot AsR_3]_4$. $CuX \cdot PR_3$ assumed to be same because isomorphous

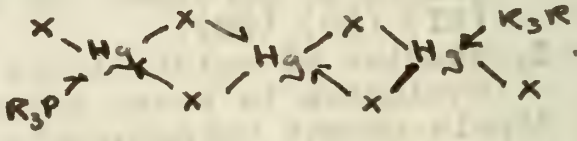


EAN of Cu = 36

3.

Tetrahedral around each Hg.

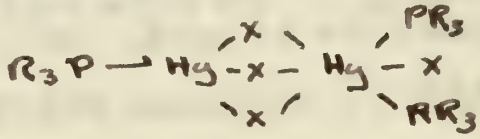
$3HgX_2 \cdot 2PR_3$ may be



no evid.

$2HgX_2 \cdot PR_3$ which is dimeric may be just an extension.

$2HgX_2 \cdot 3PR_3$ may be



??

BIBLIOGRAPHY

(1) Biltz and Keunecke, Z. anorg. allgem. chem., 147, 171 (1925).
(2) Ephraim, "A Text-Book of Inorganic Chemistry", Gurney and Jackson, London, 1926, p. 427.
(3) Holtje and Schlegel, Z. anorg. allgem. Chem., 243, 246 (1940).
(4) Holtje, ibid., 190, 253, (1930).
(5) Schwarz and Shenk, Ber., 63, 296 (1930).
(6) Fajans, Z. Electrochem. Angew. Phys. Chem., 34, 502 (1928).
(7) Klason, Ber., 28 1493 (1895).
(8) Ardell, Z. anorg. Chem, 14, 143 (1896).
(9) Angell, Drew, et. al., J. Chem. Soc. 1930, 349.
(10) Drew, et. al., ibid., 1933, 1295.
(11) Holtje, Z. anorg. allgem. chem., 209, 241 (1932).
(12) Mann, Evans, Peiser and Purdie, J. Chem. Soc. 1940, 1209.
(13) Mann and Purdie, ibid., 1940, 1230.
(14) Mann and Purdie, ibid., 1940, 1235.
(15) Mann, Purdie and Wells, ibid., 1936, 1503.
(16) Cox, Wardlaw and Webster, ibid., 1936, 775.
(17) Cox, Saenger and Wardlow, ibid., 1934, 1012.
(18) Jensen, Z. anorg. allgem. Chem., 225, 115 (1935).
(19) Mann, Purdie and Wells, J. Chem. Soc., 1937, 1830.
(20) Cox, Saenger and Wardlaw, ibid., 1934, 182.
(21) Drew and Wyatt, ibid., 1934, 56.
(22) Jensen, Z. anorg. allgem. Chem., 229, 225 (1936).
(23) Holtje, ibid., 197 93 (1931).
(24) Grossmann and von der Forst, Z. anorg. allgem. Chem., 43, 94 (1905).
(25) Rosenheim and Lowen, ibid., 37, 394 (1903); 43, 35 (1905).
(26) Mann and Purdie, J. Chem. Soc. 1936, 873.
(27) Mann and Purdie, ibid., 1935, 1549.
(28) Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry", George Routledge, London 1938, p. 107.
(29) Besson, Compt. reud., 110 80, 516 (1890).
(30) Holtje, Z. anorg. allgem. Chem., 190, 241 (1930).
(31) Lindet, Ann. Chim. Phys. 63, 11, 177 (1887).
(32) Lemoult, Compt. rend., 145, 1175 (1907).
(33) Moisson, ibid., 115, 203 (1892).
(34) Challenger, Prichard and Jinks, J. Chem. Soc., 125, 864 (1924).
(35) Arbusoff, Ber. 38 1172 (1905).
(36) Davies and Walters, J. Chem. Soc., 1935, 1786.
(37) Hertz and Davis, J. Am. Chem. Soc., 30, 1085 (1908).
(38) Tanble, Compt. rend., 132, 83 (1901).
(39) Mann and Wells, J. Chem. Soc., 1938 702.
(40) Mann and Chatt, ibid., 1938, 1949.
(41) Bennett, et. al., ibid., 1930, 1668.
(42) Elliott and Pauling, J. Am. Chem. Soc., 60 1846 (1930).
(43) Fink, Compt. rend., 115, 176 (1892); 126, 646 (1898).

THE SODIUM METAPHOSPHATES

Mary Ryan May 14, 1946

I. Introduction

The tendency of the metaphosphates to polymerize and form varied products of high molecular weight, together with the fact that these products show isomerism through different arrangement within the individual molecule so that varying constitutions may appear to have the same molecular complexity, makes these compounds the most complicated of all the acids and salts of phosphorous.

It seems incredible that there are so many problems in this field of rather limited scope which have been elucidated with so little success considering the time, interest and energy spent. The question as to structure, transformation in solution and the relationship between the various isomeric and polymeric forms is a problem often attacked, with the result that there are almost as many interpretations as there have been workers in the field.

For over one hundred years investigations have been carried out on these compounds, though for the most part they remained a laboratory curiosity until the discovery that solutions of sodium metaphosphate glass sequester calcium in a soluble complex corresponding to such a low concentration of calcium ion that the usual precipitants for calcium do not produce a precipitate. Following this discovery, industrial development and application went forward at a rapid pace and in the last six or seven years there have been hundreds of patents given on methods of preparation of soluble or insoluble sodium metaphosphate galsses.

II. Characterizing the metaphosphates

Under the general name, "metaphosphate", there are many and varied compounds and mixtures lost in the amazing lack of uniformity of naming of these salts. A single salt may be described in a half-dozen different ways depending on the theories of a half-dozen different investigators. It therefore appears that an organized manner of identification would be to characterize each compound by its method of preparation and by a limited number of reactions.

In most cases of preparations of these compounds, the condition of the product formed is entirely dependent on the method of heating, and by changing the rate of cooling of the melt, these various highly polymerized products are produced. Homogeneous products are not obtained as a rule--and melts obtained break down into unlike components when treated with water. Very soluble and very insoluble fractions as well as their own modifications are obtained so it is easy to see that the true character of the compound is not developed by water solution studies. Many specific reactions have been given as bases for the differentiation of the components of these mixtures but only in the case of crystalline soluble salts.

III. Degrees of Polymerization

A. Monometaphosphates--Pascal's salt; Maddrell's salt.
Cryoscopic measurements in water at various concentrations extrapolated to infinite dilution give an apparent molecular weight of 51.

B. Dimetaphosphates--Fleitmann's salt; Warschauer's salt.
No definite proof.

C. Trimetaphosphates--Knorre's salt.
Crystalline compound closely related to Graham's salt.

D. Tetrametaphosphates--Fleitmann's salt.
Insoluble crystalline salt, apparently a distinct compound but real nature entirely unexplained; a product of devitrification of hexametaphosphates.

E. Hexametaphosphates--Graham's salt.
Measurements of the dialysis coefficient indicate much more polymerized state than hexameric.

F. Higher polymer--Kurrol's salt.
Insoluble glass.

IV. System $NaPO_3$-$Na_4P_2O_7$

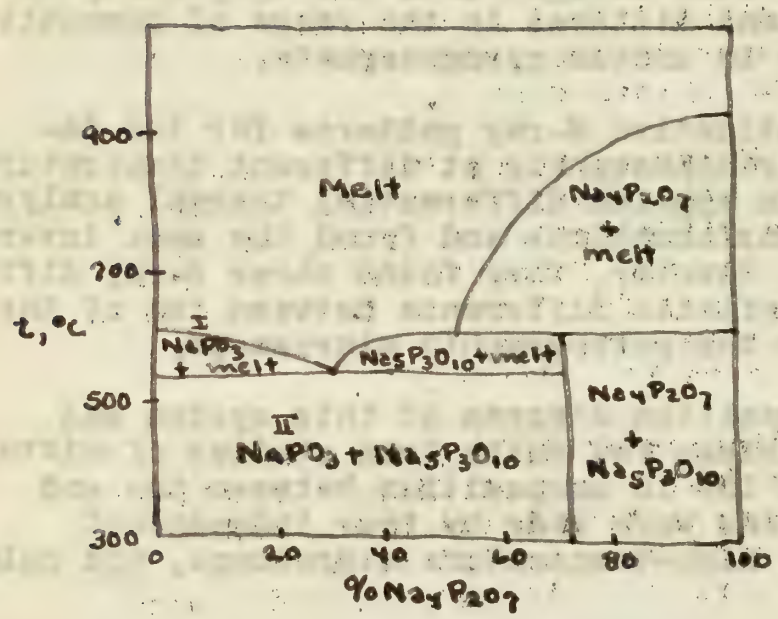
The combined evidence from thermal, optical and X-ray investigations has given close insight into the complexity exhibited by the compounds and mixtures in the range of composition from sodium metaphosphate to sodium pyrophosphate.

Boulle found two distinctive X-ray patterns for the dehydration of monosodium orthophosphate at different temperatures. Partridge, Hicks and Smith applied differential thermal analysis in order to study the transformations and found the same inversion described by Boulle. However, they found three X-ray diffraction patters, though no definite difference between two of the forms could be found with the petrographic microscope.

The temperature-composition diagram of this system was worked out by Partridge, Hicks and Smith from studies of mixtures representing intervals of 10% in composition between the end members. The investigations were made by four independent methods: thermal, X-ray, high-temperature microscope, and polarizing microscope.

From the collected data, the investigators arrived at the following conclusions:

a) Sodium metaphosphate may be obtained by thermal processes in three crystal forms.
b) Sodium pyrophosphate probably exists in five different crystal forms, but all transformations are reversible and only one form can be obtained at ordinary temperatures
c) Only one of the hypothetical polyphosphates in the system exists as a crystalline individual. This is $Na_5P_3O_{10}$, which may exist in two crystal forms at ordinary temperatures.


Melt
$Na_4P_2O_7$
+
melt
I
$NaPO_3$
+ melt
$Na_5P_3O_{10}$+melt
II
$NaPO_3 + Na_5P_3O_{10}$
$Na_4P_2O_7$
+
$Na_5P_3O_{10}$
t, °C
900
700
500
300
0
20
40
60
80
100
% $Na_4P_2O_7$

BIBLIOGRAPHY

1. Karbe and Jander, Kolloid Beihefte 54 1-146 (1942)
2. Partridge, Hicks and Smith, J. Am. Chem. Soc. 63 454-466 (1941)
3. Boulle, Compt. rend. 200 635, 832-4, 658, 1403 (1935)
4. Boulle, Compt. rend. 206 517, 915-7, 1732 (1938)
5. Beans and Kiehl, J. Am. Chem. Soc. 49 1878-1891 (1927)
6. Ephraim, "Inorganic Chemistry" Nordeman Publishing Company, New York 1943, pp. 727-730
7. Yost and Russell, "Systematic Inorganic Chemistry" Prentice-Hall, 1944, pp. 210-224

STABILITY OF CHELATE COMPOUNDS

Hung Kao May 14, 1946

I. The method

Recently two studies have been published (1,2) on the influence of certain structural factors upon the stability of chelate compounds of divalent copper in a more or less quantitative manner. The second paper (4) in this series will be published in the J. Am. Chem. Soc. for this month. The stability of chelates is defined with respect to the reaction

$$Cu^{++} + 2Ke^{-} \rightleftharpoons CuKe_2 \qquad (A)$$

where Ke^{-} represents the anion of a β diketone or a O-hydroxy aromatic aldehyde.

The method used consists of determining the H^{+} concentration of a solution containing known quantities of copper, chelating substance, acid and base. Fifty percent dioxane-water solutions of $Cu(ClO_4)_2$, HKe(0.02M) and $HClO_4$ (0.02M) were titrated with aqueous sodium hydroxide. The total copper present is of the order of 10^{-3} M. It was found that the equilibrium was not as simple as represented by (A). J. Bjerrum's method of calculation was then used. Assume that the reaction goes in steps

$$Cu^{++} + Ke^{-} \longrightarrow CuKe^{+} \quad (B)$$

$$CuKe^{+} + Ke^{-} \longrightarrow CuKe_2 \quad (C)$$

and $$K_1 = \frac{(CuKe^{+})}{(Cu^{++})(Ke^{-})} \qquad K_2 = \frac{(CuKe_2)}{(CuKe^{+})(Ke^{-})}$$

at equilibrium we have:

$$T_{Cu^{++}} = Cu^{++} + CuKe^{+} + CuKe_2 \qquad (D)$$

$$T_{HKe} = HKe + Ke^{-} + CuKe^{+} + 2CuKe_2 \qquad (E)$$

$$CuKe^{+} + 2Cu^{++} + Na^{+} + H^{+} = ClO_4^{-} + OH^{-} + Ke^{-} \qquad (F)$$

$$K_D = (H^{+})(Ke^{-})/(HKe) \qquad (G)$$

$$ClO_4^{-} = A + 2T_{Cu^{++}} \qquad (H)$$

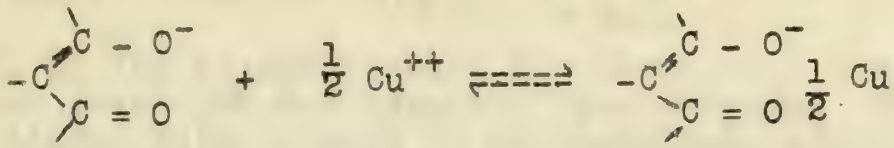
From these equations we obtain:

$$\bar{N} = (Na^{+} - A + H^{+})/T_{Cu^{++}} \qquad (I)$$

Where $\bar{N}$ is the average number of Ke^{-} bound to Cu^{++}, plot $\bar{N}$ against $P\underline{K}e^{-}$ and K_1 and K_2 determined approximately from the curve at $\bar{N} = 0.5$ and 1.5 respectively. At $\bar{N} = 1.0$ $\frac{1}{Ke^{-}}$ gives an average constant K_{av} such that $(K_{av})^2 = K_1 K_2$.

II. Results of determination

The value K_{av} can be taken in a first approximation to represent the equilibrium constant of the general reaction



The accuracy of the data as yet does not warrant any discussion of the difference between K_1 and K_2. Another limitation imposed by the character of the data concerns the absolute values of the constants themselves. Until the temperature coefficients are determined and by that the heats and entropies of the reactions, we will be concerned only with the relative values of the constants.

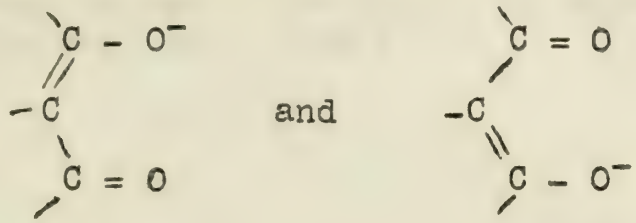
Table I*

Compound	K_1	K_2	K_{av}	K_D
solicylaldehyde	$10^{7.5}$	$10^{5.8}$	$10^{6.6}$	$10^{-9.5}$
3-N-propyl	$10^{8.0}$	$10^{6.3}$	$10^{7.7}$	$10^{-9.6}$
5-methyl	$10^{7.7}$	$10^{6.0}$	$10^{6.8}$	$10^{-9.7}$
4,b-dimethyl	$10^{8.3}$	$10^{6.7}$	$10^{7.5}$	$10^{-10.4}$
3-ethoxy	$10^{7.95}$	$10^{5.85}$	$10^{7.1}$	$10^{-9.4}$
3-nitro	$10^{4.9}$	$10^{3.4}$	$10^{4.2}$	$10^{-6.0}$
3-fluoro	$10^{6.6}$	$10^{4.9}$	$10^{5.8}$	$10^{-7.8}$
2-hydroxy-naphthaldehyde-1	$10^{7.6}$	$10^{8.0}$	$10^{6.8}$	$10^{-8.4}$
2-hydroxy-naphthaldehyde-3		est	$10^{5.8}$	$10^{-9.9}$
acetyl-acetone	$10^{9.0}$	$10^{8.1}$	$10^{8.75}$	$10^{-9.7}$
Tri fluoro acetyl acetone	$10^{6.3}$	$10^{5.9}$		$10^{-6.7}$
Furoyl acetone	$10^{8.7}$	$10^{8.2}$		$10^{-9.3}$
Benzoyl acetone			$10^{9.0}$	$10^{-9.8}$
C-methyl benzoyl acetone	$10^{8.5}$	$10^{7.3}$	$10^{7.7}$	$10^{-11.8}$
Aceto acetic ester	$10^{8.4}$	$10^{6.5}$	$10^{7.5}$	$10^{-11.2}$

* The first seven are derivatives of salicylaldehyde the next two are derivatives of β naphthal, the next five are derivatives of acetone.

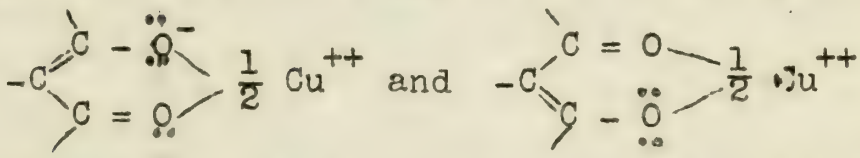
III. Conclusion

A plot of log K_D against log K_{ay} shows that the compounds fall into at least two and possibly four classes. Within each class the linear relationship is approximately followed and the slopes of two lines obtained are very nearly the same. The forces responsible for holding the copper in the chelate are made up of at least two different components, one which is of the same character for both copper and hydrogen while the other plays a different and far greater part in the bonding of copper than it does in the bonding of hydrogen. The latter is due to enolate resonance between

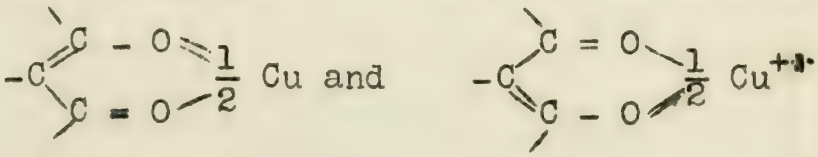


E_1 and E_2

Thus the Cu^{++} in the chelate may either form a homopolar bond as



or a six-membered ring is involved in the chelate as



IV Evidence from kinetic studies

The rates of exchange of a series of copper chelate compounds with copper ion, the copper ion being marked by containing a radioactive copper isotope

$$Cu^{++}Ke_2 + Cu^{++*} \longrightarrow Cu^{++*}Ke_2 + Cu^{++}$$

have been measured (2) and it has been found that the reaction is bimolecular in the chelate and the copper acetate. The remarks and conclusions concerning the effect of the organic structure upon the stability of the chelates as determined from equilibrium studies can be applied here. This may be seen in the following pair of compounds measured under the same conditions

Acetylacetone ethylenediimine $T_{\frac{1}{2}}$ = 37 hrs.

Salcylaldehyde ethylenediimine $T_{\frac{1}{2}}$ = 2.1 hr.

References

(1) Calvin and Wilson J. Am. Chem. Soc. 67 2003 (1945)

(2) Calvin and Duffield, ibid 68 557 (1946)

(3) J. Bjerrum: "Metal Ammine Formation in Aqueous Solution" P. Haase and Son. Copenhagen. (1941)

(4) Calvin and Bailes, J. Am. Chem. Soc. 68 May (1946)

(5) Branch and Calvin: The Theory of Organic Chemistry Prentice-Hall Inc. (1941)

THE CARBIDES

Ann Lippincott May 21, 1946

I. Types of carbides

The compounds of metals and carbon are of two kinds, the refractory type and the salt-like type.

The refractory type is formed by the elements of groups IV, V, and VI of the periodic system. They have many of the properties of true metals: high electrical conductivity with a negative temperature coefficient, superconductivity, and weak paramagnetism. They do not react with water or with dilute acids.

The salt-like carbides are formed by the alkaline earths, the alkalies, the rare earths, and the iron group. They are colorless, transparent, crystalline solids, non-conductors of electricity. They are decomposed by water or dilute mineral acids, with the formation of hydrocarbons. The exact products of the hydrolysis depend upon the structure of the compound, and the salt-like carbides may be classified according to these products:

a) Those yielding methane--Be_2C, Al_4C_3

b) Those yielding acetylene--Na_2C_2, K_2C_2, CaC_2, SrC_2, BaC_2, Au_2C_2, Ag_2C_2

c) Those forming mixtures
   1) Chiefly methane and hydrogen--Fe_3C, Mn_3C, Ni_3C
   2) Chiefly acetylene--UC_2, LaC_2, NdC_2, ThC_2, MnC_2

II. Structure

The refractory carbides are interstitial compounds which have a structure determined by the metallic atoms. The non-metallic atoms are packed into the interstices between the metallic ones. The metallic properties are therefore explained by the fact that their structure is primarily that of the metal.

The salt-like carbides possess ionic lattices (hence their name). The cations are in the interstices between the close-packed carbon anions. The nature of these carbides depends mainly upon two factors, the first of which is the electro-positiveness of the metal from which it is formed. The salt-like character of the compound decreases as the electropositiveness of the metal from which it is formed decreases. In the series Be_2C, Al_4C_3, SiC, the most salt-like is Be_2C, and SiC is of an almost completely homopolar character.

The second factor is the size of the cation, in conjunction with its valency. The close packed structure of the anions allows two "tetrahedral" cavities for occupation by cations for each anion present. If valence considerations require more than two cations, there is no room for them. Thus, there are no "methane" salts of the alkali metals such as Na_4C. Divalent

cations of the alkaline earths could be present, but they are large enough that the anion lattice would be deformed. The carbon lattice seems, therefore, to break up into distinct $C_2^{=}$ groups, and the known alkali and alkaline earth carbides are of the type Na_2C_2 or CaC_2. It is because these compounds contain carbon pairs (acetylide ions) that their hydrolysis product is acetylene.

The rare earth carbides, which give chiefly acetylene on hydrolysis, are similar. The other products vary with the conditions of decomposition, but are chiefly other saturated and unsaturated hydrocarbons. The irregular products are believed to be formed as a result of the change of the metal from the bivalent to its ordinary tri or tetravalent state.

If methane is a hydrolysis product, as with Be_2C and Al_4C_3, the carbide has a lattice in which the carbon atoms are separated from each other. The hydrogen which is set free then reacts with the carbon atoms separately, rather than in pairs.

Magnesium carbide is not similar to any of the carbides which have been mentioned. Its formula is Mg_2C_3, and it yields allylene on hydrolysis, which implies that C_3^{-4} exists in the crystal lattice.

The iron group carbides are intermediate between the refractory and the salt-like carbides. Structurally they are like the refractory. Chemically they are not as stable, and not as perfectly metallic. There is serious distortion of the metal lattice unless

$$\frac{\text{radius of metal}}{\text{radius of C}} > 1.7 \text{ A}$$

That is, since the radius of C is 0.77Å, the metallic atomic radius must be greater than 1.3Å to avoid distortion. The radii of all the iron group metals are smaller than this limiting value. Therefore, while sharing the metallic characteristics of the interstitial compounds, they have modified properties and crystal structures distinct from those of the metals.

III. Preparation

Moissan was the first to do extensive work on the carbides, and he prepared them by heating a mixture of the metal or its oxide or carbonate with carbon and heating the mixture in an electric furnace. Heating the metal in acetylene is a less satisfactory method of preparation.

Calcium carbide, used for making acetylene and in the manufacture of cyanamide, and silicon carbide (carborundum) are manufactured commercially, and the methods used are essentially the same as those of Moissan.

BIBLIOGRAPHY

1. Emeleus and Anderson; "Modern Aspects of Inorganic Chemistry," Routledge, London, 1938, p. 453
2. Lebeau, P.; Compt. rend., 121, 496 (1895)
3. de Mahler, E, Bull. soc. chim., (IV) 29, 1071 (1921)
4. Moissan, H, Ann. chim. phys., (7) 9, 302 (1896)
5. Moissan and Etard, Compt. rend., 22, 593 (1896)
6. Moissan and Lenfeld, ibid, 22, 651 (1896)
7. Myers and Fischel, J. Am. Chem. Soc. 67, 1962 (1945)
8. Ruff, O., Z. Elektrochem, 24, 157 (1918)
9. Schmahl, N. G., ibid, 40, 68 (1934)
10. Schmidt, J., ibid, 40, 170 (1934)
11. von Stackelberg, Z. physik. Chem. (B) 27, 53 (1934)

THE FLUORINATION OF NON-POLAR CHLORIDES AND THE THERMOCHEMISTRY OF HALOGEN EXCHANGE REACTIONS

M. M. Woyski May 21, 1946

The halogen exchange reaction is the most important method for the preparation of the less common metal and non-metal fluorides. Although a large number of such reactions have been observed the course of halogen exchange reactions in general has not been predicted.

Table 1 gives the heats of formation of a number of chlorides and fluorides and the differences (per equivalent) of these quantities. The algebraic difference of these values for any two chloride-fluoride 'couplets' gives the enthalpy changes for the halogen exchange reaction. These enthalpy changes may be used in lieu of free energy data for calculation of equilibrium constants since the entropy of exchange reactions (except those involving some of the lighter elements) is negligibly small.

Table 1 may be considered as a scale of fluorinating agents in decreasing order of thermodynamic activity.

For lack of thermal data most of the non-metal chloride-fluoride couplets cannot be placed on this scale. That the chlorides (with some exceptions, e.g. sulfuryl) are readily fluorinated by antimony or calcium fluorides indicates that they are low on the list.

Experimental Work

1. Anhydrous hydrogen fluoride, at 25°C., is capable of fluorinating several of the non-polar chlorides, namely, phosphoryl chloride, phosphorus trichloride, phosphorus pentachloride, thionyl chloride, chlorosulfonic acid and silicon tetrachloride.

2. Anhydrous hydrogen fluoride reacts with sulfuryl chloride to a very slight extent, if at all. It is not decided whether this is due to equilibrium conditions or to chemical inertness of sulfuryl chloride.

3. The relative rates of reaction of the several non-polar chlorides with anhydrous hydrogen fluoride have been observed roughly.

4. Intermediate products of the fluorination of phosphoryl trichloride by hydrogen fluoride ($POCl_2F$ and $POClF_2$) can be isolated in good yield by proper control of the conditions of the reaction.

5. Hydrogen fluoride exhibits high chemical reactivity as a fluorinating agent. It reacts with all chlorides with which the exchange reaction has been shown to be thermodynamically possible.

6. Limited evidence indicates the non-polar fluorides to be comparatively unreactive in exchange reactions up to a temperature of about 100°C.

7. Fluorosulfonic acid reacts slowly with phosphoryl chloride, phosphorus trichloride and thionyl chloride at about 100°C. with formation of fluorine compounds but the reactions are not straight-forward exchange reactions. Phosphorus trichloride, PCl_3, for example, give rise to phosphoryl trifluoride, POF_3.

8. A study of halogen exchange reactions involving hydrogen fluoride and the non-polar chlorides in the gas phase was not successful.

Reference: Ph.D. Thesis. M. M. Woyski
University of Illinois, 1946

(At Approximately 25°)

$-\Delta H°$ calories/mole Chloride	Fluoride	Couplet	$\Delta H°HCl - \Delta H°MF$ calories/equivalent
30,300	48,700	$AgF(s) = AgCl(s)$	18,400
106,320	131,680	$CsF(s) = CoCl(s)$	25,400
105,080	133,240	$RbF(s) = RbCl(s)$	28,200
104,361	134,510	$KF(s) = KCl(s)$	30,150
33,800	163,000	$1/4\ CF_4(g) = 1/4\ CCl_4(l)$	32,300
25,900	163,000	$1/4\ CF_4(g) = 1/4\ CCl_4(g)$	34,300
92,149	162,490	$1/2\ CdF_2(s) = 1/2\ CdCl_2\ (s)$	35,200
84,874	156,000	$1/2\ PbF_2(s) = 1/2\ PbCl_2\ (s)$	35,600
74,950	111,600	$NH_4F(s) = NH_4Cl(s)$	36,650
98,590	172,700	$1/2\ ZnF_2\ (s) = 1/2\ ZnCl_2\ (s)$	37,100
98,330	135,950	$NaF(s) = NaCl\ (s)$	37,600
53,400	131,800	$1/2\ CuF_2(s) = 1/2\ CuCl_2\ (s)$	39,200
75,000	157,500	$1/2\ NiF_2(s) = 1/2\ NiCl_2\ (s)$	41,250
205,280	287,900	$1/2\ BaF_2(s) = 1/2\ BaCl_2\ (s)$	41,300
91,400	216,600	$1/3\ SbF_3(s) = 1/3\ SbCl_3\ (s)$	41,700
75,900	160,700	$1/2\ CoF_2(s) = 1/2\ CoCl_2\ (s)$	41,900
22,060	64,000	$HF\ (g, ideal) - HCl(g)$	41,950
88,400	216,600	$1/3\ SbF_3(s) = SbCl_2(l)$	42,700
197,870	289,000	$1/2\ SrF_2(s) = 1/2\ SrCl_2(s)$	45,550
		$1/3.3\ (HF)_{3.3}(g.\ 745\ mm) = HCl\ (g)$	47,300
97,650	145,570	$LiF(s) = LiCl(s)$	47,900
190,600	290,200	$1/2\ CaF_2(s) = 1/2\ CaCl_2$	49,800
150,100	360,100	$1/4\ SiF_4(g) = 1/4\ SiCl_4(l)$	52,500
94,600	256,900	$1/3\ BF_3(g) = 1/3\ BCl_2(l)$	54,100
166,800	329,000	$1/3\ AlF_3(s) = 1/3\ AlCl_3(s)$	54,100
142,500	360,100	$1/4\ SiF_4(g) = 1/4\ SiCl_4(g)$	54,100
153,300	263,800	$1/2\ MgF_2(s) = 1/2\ MgCl_2(s)$	55,250
88,300	256,900	$1/3\ BF_3(g) = 1/3\ BCl_3(g)$	56,200
133,000	329,000	$1/3\ AlF_3(s) = 1/3\ AlCl_3(g)$	65,300

THE STEREOCHEMISTRY OF COMPLEX COMPOUNDS CONTAINING ORGANIC MOLECULES

Hans B. Jonassen May 28, 1946

On the basis of the work of Jaeger (1) and Smirnoff (2) Bailar (3) predicted in 1936 that complex inorganic compounds might be used to resolve optically active bases. Several attempts (4) in this laboratory to bring about such resolutions met with failure.

However, the experimental evidences obtained by Huffman (4) indicated that in the reaction of d-tartrato bis-ethylenediamino cobaltic chloride and calcium nitrite an active form of the dinitro bis-ethylenediamino cobaltic chloride complex was formed. Huffman also found that he never was able to obtain more than 40% of the theoretical yield; under no conditions was he able to increase this by more than about two percent. These data seem to indicate that the two forms of the d-tartrato react at different rates.

It was decided to study the reaction of d-tartrato bis-ethylenediamino cobaltic bromide with ethylenediamine since in the presence of activated charcoal (5) trisethylenediamino cobaltic bromide is formed without the necessity of heating. However, since the bis-ethylenediamino cobalt complexes racemize very easily whereas the bis-levo-propylenediamino complexes are so stable that they can be subjected to a very severe treatment without racemization, this study also includes the reaction of bis-levo-propylenediamino cobaltic bromide with levo-propylenediamine. Huffman's work with this complex also indicated that the two forms of the tartrato complex react at different rates when the dinitro-bis-levo-propylenediamino complex is formed.

EXPERIMENTAL

The resolved complexes used in this study were available from laboratory stock; the other complexes were made according to methods found in the literature.

Preliminary tests on resolved tris-ethylenediamino cobaltic bromide showed that no racemization of the active complex occurred either upon shaking with Norite (activated charcoal) or upon heating the solutions at 50°C for more than 24 hours.

Studies of the reaction of d-tartrato bis-ethylenediamino cobaltic bromide and 69% ethylenediamine showed that the tris-ethylenediamino cobaltic complex formed under these conditions was a racemic mixture. The reaction of this complex with 69% of ethylenediamine in the absence of Norite, however, produced an optically active form of the tris-ethylenediamino cobaltic bromotartrate. The yield was 140% of the theoretical one which showed that 40% of one form has been rearranged to the other form during the reaction. Measurements of rotation on the filtrat showed that the originally levorotatory complex increased in negative rotation as the tris-ethylenediamino cobaltic bromotartrate was removed.

The data obtained from the reaction of dl-tartrato bis-levo-propylenediamino cobaltic chloride and levo propylenediamine indicate that a partial resolution has occurred. The reaction mixture is heated at 70° C for one hour. Upon pouring this solution into ice cold methyl alcohol tris-levo-propylenediamino cobaltic chlorotartrate is precipitated and is removed by filtration (precipitate 1). The methyl alcohol filtrate is returned to the steamcone and evaporated to dryness at 70°C. (precipitate II). The precipitates (I and II) are treated with lead nitrate after several recrystallizations and the insoluble lead tartrate is removed by filtration. It is suspended in water and saturated with hydrogen sulfide. The lead sulfide is filtered and the excess of hydrogen sulfide removed from the filtrate by boiling. The filtrate is then evaporated in a stream of air. The tartaric acid obtained from precipitate I shows a high positive rotation whereas that from precipitate II has a high negative rotation. The yields of the two fractions: Fraction 1 75%, fraction II 80% of the theoretical.

DISCUSSION

The high yield in the partial resolution of tris-ethylenediamino cobaltic bromotartrate obtained from the reaction of d-tartrato bis-ethylenediamino cobaltic bromide and ethylenediamine can be explained only if it is assumed that the following reactions take place:

I) dextro $Coen_2$d-tart Br $\rightleftharpoons$ levo $Coen_2$d-tart Br
II) dextro $Coen_2$d-tart Br +en* ---→ dextro $Coen_3$ Br d-tart
III) levo $Coen_2$d-tart Br +en ---→ levo $Coen_3$ Br d-tart

Equilibrium I is displaced to the right as indicated by the negative rotation of the original bisethylenediamino complex. As ethylenediamine is added and the reaction mixture is shaken tris-ethylenediamino cobaltic bromotratrate is formed which has a high positive rotation. This seems to indicate reaction II is occurring predominantly in the reaction mixture. This displaces equilibrium I to the left and more of the dextro complex is formed this change in the equilibrium concentrations will produce an increase in the negative rotation of the original complex remaining in the solution. Reaction III is also occurring in the mixture but at a much slower rate. This is shown by the fact that the rotation of the tris-ethylenediamino complex formed is slightly less than that of the completely resolved complex.

This is an example of resolution by the "equilibrium method" described by McKenzie and Smith (6) and others for compounds containing asymmetric carbon atoms. This is the first time it has been used for a partial resolution of inorganic complexes.

The studies with dl-tartrato bis-levo-propylenediamino cobaltic chloride and levo propylenediamine show that the first tartrate ion removed from the complex consists mostly of the d-tartrate ion. Complete evaporation of the reaction mixture brings about displacement of the l-tartrate ion from the remainder of the complex. It is thus possible to effect a partial reso-lution of the two forms of tartaric acid.

*abbreviation for ethylenediamine.

SUMMARY

1) The first example of partial asymmetric synthesis by the "equilibrium method" is described for inorganic complexes. It involves the formation of dextro tris-ethylenediamino cobaltic bromide by the displacement of the d-tartrate ion from d-tartrato bis-ethylenediamino cobaltic halides by ethylenediamine.

2) A reaction mechanism for this resolution is proposed.

3) It is shown that it is possible to resolve racemic tartaric acid by means of the displacement of the active tartrate ion from dl-tartrato bis-levo-propylenediamino cobaltic chloride by levo propylenediamine

4) It may be possible that this method of resolution may be applied to determine the absolute configuration of optically active groups which coordinate.

5) Possible application of this method for the resolution of other racemic acids or amines is discussed.

6) The advantages and disadvantages of this method over other methods of resolution are discussed.

BIBLIOGRAPHY

1) Jaeger, Optical Activity and High Temperature Measurements, McGraw-Hill Book Co., 1930, p. 143-156.
2) Smirnoff, Helv. Chim. Acta. 3, 177, (1929).
3) Bailar, Chem. Rev. 19, 67, (1936).
4) Balthis, Thesis, University of Illinois, 1934; Huffman, Thesis, University of Illinois, 1936; Stiegman, Thesis, University of Illinois, 1937.
5) Bailar and Work, J. Am. Chem. Soc. 67, 176 (1945).
6) McKenzie and Smith, Ber. 58, 899, (1925).

THE REDUCTION POTENTIALS OF SOME INORGANIC COORDINATION COMPOUNDS

James V. Quagliano May 28, 1946

The purpose of this investigation was to make a quantitative study of the reactions that take place at the dropping mercury electrode when a solution of hexammine cobaltic ion is electrolyzed in the presence of a large excess of various inert salts, and establish the conditions under which the reduction of this ion is reversible. Half-wave potentials of oxidation-reduction reactions obtained at reversible conditions have, over those which are irreversible, the great advantage of a thermodynamic significance which can be related to the ordinary standard potentials. Furthermore, the quantitative measurements can be applied advantageously to the study of the strength of the bonds between the central atom and the coordinating molecules, to the determination of diffusion coefficients of complex ions (and molecules), to obtain information about optimum conditions in the preparative work of inorganic complexes, and to the study of inorganic systems that can not be studied by classical methods.

PREVIOUS INVESTIGATIONS

Most of the complex ions which have been studied by the polarographic method were prepared by the addition of the metallic ion to a large excess of the complex forming substance, which also acted as the supporting electrolyte. Brdicka found that the hexammine cobaltous ion is oxidized by dissolved oxygen in ammonical solutions and the resulting hexammine cobaltic ion produces a double polargraphic wave. The analysis of solutions prepared by dissolving pure complex cobaltic salts was made recently.

APPARATUS AND EXPERIMENTAL METHODS

The principle of the method of determining the half-wave potentials is illustrated by the following description of some preliminary experiments. Purified hydrogen gas was passed into the electrolysis cell (containing the solution to be analyzed) for about twenty minutes to displace all of the dissolved oxygen, at which time the flow was discontinued. The potential of the dropping mercury electrode was increased in increments of 0.05 volt, and the amperage reading was recorded from a Fisher Electropode.

EXPERIMENTAL RESULTS

The effect of gelatin and octyl alcohol in the reduction of the hexammine cobaltic ion at the dropping electrode are very interesting for they not only eliminate the incipient maximum but also displace the wave to more negative potentials. The presence of agar from concentrations of 1.9×10^{-5} to 1.4×10^{-4} per cent produce no change in the half-wave potential of the hexammine ion.

The half-wave potentials and the diffusion currents of the hexammine cobaltic ion were obtained in the presence of six different supporting electrolytes. The half-wave potentials are less negative in solutions of the "indifferent" electrolytes which have little (or no) tendency to coordinate (viz., nitrate and perchlorate). The half-wave potential in the presence of acetate ions is shifted to a more negative value by 0.1 volt, and that in the presence of sulfate ions is more negative by 0.2 volt. A series of experiments was made to determine the effect of an increase in concentration of the supporting electrolytes and the presence of ammonia on the reduction curves. A 0.002 per cent solution was found to be the minimal concentration of sodium methyl red which would suppress the maximum.

DISCUSSION

The displaced curves rise more steeply in the solutions which contain the gelatin, and gelatin and octyl alcohol. The adsorbed gelatin and octyl alcohol cause the potential drop to occur in a very small region of solution near the mercury surface. If the potential fall nearly all occurs in the adsorbed layer, no deformation of ions can occur. Normally, the central atom (Co) is attracted by the electrode, and distortion of the reducible ion (hexammine cobaltic) occurs whereby the central ion is attracted toward the electrode and the coordinating groups (NH_3) distorted away from the electrode, but this is determined by the potential gradient in the solution. In the presence of gelatin a higher potential is necessary.

Although a negative slope in the diffusion current does not occur in the decomposition curve of the hexammine cobaltic ion in the presence of sulfate ions, the presence of a trace (0.002 per cent) of sodium methyl red decreases the diffusion current. This indicates that a new type of maximum behavior takes place in complex cobaltic solutions, namely, that the stirring effect in the solution at the region of the mercury drop which accompanies the maxima continues with increasing applied potentials.

In the polarographic experiments the concentrations of the indifferent electrolytes are at least one-hundred times that of the ion undergoing reduction. Most likely the anions of the supporting electrolyte are bound by ionic bonds in a second sphere about the hexammine cobaltic ion.

SUMMARY

1. The polarographic reduction of the hexammine cobaltic ion in the presence of chloride, nitrate, perchlorate, acetate, and sulfate ions and ammonia has been studied in the range of -0.05 to -0.8 volt.

2. Capillary active substances such as gelatin and octyl alcohol markedly shift the half wage potentials of the hexammine cobaltic ion to more negative potentials. In the presence of these substances a stirring effect which accompanies the maximum continues with increasing applied potentials.

3. The polarographic analysis of the hexammine cobaltic ion can be made in the presence of methyl red to suppress the maximum.

4. The hexammine cobaltic ion is present as the central ion of the super complex in the media of chloride, nitrate, perchlorate, acetate and sulfate ions. In the presence of sulfate and acetate ions, in contrast to the other media, fairly stable "super-complexes" are formed which results in shifting the half -wave potentials to more negative values, and to lowering the diffusion currents.

Reference: Ph.D. Thesis
James V. Quagliano
University of Illinois, 1946

THE PREPARATION AND PROPERTIES OF SOME PLATINUM AMINES

J. A. Mattern June 4, 1946

Although it is generally believed that chelating groups such as ethylenediamine are unable to reach across trans positions in the coordination sphere of a metal, there is no reason to suppose that a chelating group of sufficient size cannot, under the proper conditions, coordinate across trans positions. However, previous attempts to prepare simple chelate rings of seven or more members have given inconclusive or negative results. The general procedure has been to treat a metallic salt or complex with a large diamine, such as pentamethylenediamine, in the hope that both amine groups will coordinate to the metallic ion. This reaction presents difficulties, however. Although there is an excellent chance that one amine group in the course of its motion will encounter and coordinate to a metallic ion, the probability that the second amine group will reach and coordinate to the same metallic ion is rather small because the motion of this second amine group is comparatively unrestricted. Accordingly, one or more of the following reactions takes place instead of chelation: (1) The precipitation of the metal as an insoluble hydroxide (2) the formation of polymer-like materials by coordination of one diamine molecule to two different metallic ions (3) the filling of the coordination sphere with more strongly chelating groups as, for example, the formation of $[Co\ en_3]\ Cl_3$ from $[Co\ en_2\ Cl_2]\ Cl$ when it reacts with long chain diamines. Little work has been done to ascertain whether or not these side reactions can be avoided by the use of nonaqueous solvents or the use of catalysis.

Diethylenetriamine, although its end amine groups are just as far removed from each other as those of pentamethylenediamine, is readily able to place its two end amine groups in trans positions of the coordination sphere because coordination of the center amine group greatly resticts the motion of an uncoordinated end group and thereby increases the probability of coordination. This amine, therefore, coordinates preferentially as a tridentate group. Mann (1), in fact, has found it difficult to prepare a bidentate compound of diethylenetriamine by direct means.

If it is possible to remove the middle amine from the coordination sphere of such a tridentate complex, and eight-membered chelate ring may be produced which spans trans coordinate positions. Two possible methods for doing this are: (1) to take advantage of the change of coordination number with change of valence which some metals exhibit and (2) to replace one group with another in the coordination sphere. Chernyaev and Fedorova (2) used both of these methods to prepare monodentate compounds of ethylenediamine from the corresponding bidentate compounds.

The tridentate compound used in this investigation was 2-chloro-1,6-diammine-3,4,5-diethylenetriamine platinic chloride which was prepared by the following series of reactions:

(1) $H_2PtCl_6 \xrightarrow{\Delta} PtCl_2 + 2HCl + Cl_2$

(2) $PtCl_2 + 4NH_3 \longrightarrow [Pt(NH_3)_4]Cl_2$

(3) $[Pt(NH_3)_4]Cl_2 \xrightarrow{\Delta}$ <u>trans</u> $[Pt(NH_3)_2Cl_2] + 2NH_3$

(4) <u>trans</u> $[Pt(NH_3)_2Cl_2] + Cl_2 \longrightarrow$ <u>trans</u> $[Pt(NH_3)_2Cl_4]$

(5) <u>trans</u> $[Pt(NH_3)_2Cl_4] +$ dien $\longrightarrow$

<u>trans</u> $[Pt\ dien\ (NH_3)_2Cl]Cl_3$

Reaction (1), which was used by Kharasch and Ashford (3), was found to be much easier to carry out than reduction by sulfur dioxide or other means. Reaction (2) was improved by the use of Norite charcoal as a catalyst which eliminated troublesome by-products. Reaction (3) was conducted at 230-240° C. at a pressure of 120-140 mm. of mercury. Reaction (5) was conducted by shaking the theoretical amount of diethylenetriamine with <u>trans</u> $[Pt(NH_3)_2Cl_4]$ in the presence of Norite charcoal at room temperature. The use of a higher temperature resulted in reduction to $[Pt(NH_3)_2Cl_2]$ and the use of excess amine produced the <u>bis</u>-diethylenetriamine complex $[Pt\ dien_2]Cl_4$.

Platinum was chosen for this investigation because (1) coordination compounds of this metal generally show a coordination number of six in the tetravalent state and a coordination number of four in the divalent state and (2) coordination compounds of this metal do not usually show a tendency to rearrange. Assuming that no rearrangement took place which would involve breaking of the strong platinum-ammonia bond, the diethylenetriamine in $[Pt\ dien\ (NH_3)_2Cl]Cl_3$ has its two end amine groups <u>trans</u> to each other and its middle amine group <u>trans</u> to a chloride group. There are, therefore, two factors which aid the expulsion of the secondary amine group from the coordination sphere, namely: (1) the <u>trans</u> effect and (2) the decreased stability of secondary amine coordinate bonds in comparison with those of primary amines. Moreover, the chloride group, which is not as firmly coordinated to platinum as nitrogen, is also easily expelled from the coordination sphere. Reduction of $[Pt\ dien\ (NH_3)_2Cl]Cl_3$ may, therefore, produce a planar compound containing bidentate diethylenetriamine attached to <u>trans</u> positions of the coordination sphere. Rearrangement is not expected in the course of this reaction if the groups which leave the coordination sphere are <u>trans</u> to each other.

The reduction of $[Pt\ dien\ (NH_3)_2Cl]Cl_3$ by electrolysis was found to give a mixture which, upon reprecipitation, indicated a N/Pt ratio of 4.6 and a Cl/Pt ratio of 2.6. After the reprecipitation process had been repeated four times these ratios had dropped to 4.1 and 2.1 respectively. Titration of the reduction product of $[Pt\ dien\ (NH_3)_2Cl]Cl_3$ with base showed that approximately one-sixth of the chlorine was present as available hydrochloric acid. This suggests that the reduction product contains both bidentate and tridentate compounds of diethylenetriamine, the former being readily converted to the latter according to the equation:

$[Pt\ dien\ HCl\ (NH_3)_2]Cl_2 \longrightarrow [Pt\ dien\ NH_3]Cl_2 + NH_4Cl$

If the bidentate compound contains primary amine groups joined to <u>trans</u> positions of the coordination sphere, this reaction is highly probable.

The reduction product of $[Pt\ dien\ (NH_3)_2\ Cl]Cl_3$ was found to react readily with hydrochloric acid to produce trans dichlorodiammine platinum. Identification as the trans form was made by ultraviolet absorption studies and by the preparation of the bisoxalato derivative $[Pt\ (NH_3)_2\ (HC_2O_4)_2]$ according to Grinberg (4). It is difficult to believe that the trans dichloro salt would be obtained from a tridentate compound of diethylenetriamine except under very severe conditions. Production from a bidentate compound would require that diethylenetriamine span trans positions unless rearrangement takes place.

Further work is needed to ascertain whether or not such a bidentate compound can be isolated in pure form. It is suggested that the use of diethylenetriamine or similar compound containing a somewhat poorer coordinating group in the center may, by the method outlined, prove useful in synthetic work.

References

1. Mann, F. G., J. Chem. Soc., 1934, 466

2. Chernyaev, I. I. and Fedorova, A. N., Ann. secteur platine, Inst. chem. gen. (U.S.S.R.), No. 14, 9-18 (1937)

3. Kharasch, M. S. and Ashford, T. A., J. Am. Chem. Soc. 58, 1733 (1936)

4. Grinberg, A. A., Helv. Chim. Acta., 14, 455 (1931)

A STUDY OF THE OLEFIN TO PLATINUM BOND

A. L. Oppegard June 4, 1946

I. Introduction

Although many metals (Pt, Pd, Fe, Ir, Al, Zn, Cu, Ag and Hg) will form coordination compounds with olefins and olefinic substances, those formed with platinum are the most stable and are best characterized. The fact that the olefins do not have a free pair of electrons has aroused considerable speculation as to the nature of the bond that is formed, for the compounds are very similar chemically to other types of complex salts. Many theories have been advanced, none of which is entirely satisfactory. The object of this research has been to establish certain important facts about these compounds which have remained in doubt.

The platinum-olefin complex compounds can be divided into two distinct series, $(PtCl_2 \cdot uns)_2$ and $M(PtCl_3 \cdot uns)$. The former are non-ionic compounds soluble in organic solvents and dissolving in aqueous solutions of MCl to form the second series which is ionic. They can be made from platinic or platinous compounds. The two most common methods of preparation are 1) Anhydrous platinic chloride in an anhydrous solvent such as glacial acetic acid plus the olefin, 2) Potassium chloroplatinite in alcohol-water solution plus the unsaturated substance. Hydrocarbons, unsaturated alcohols, acids, aldehydes and esters can form coordination compounds.

The stabilities of the compounds vary widely and depend on the nature of the olefin. Ethylene, styrene and trans-stilbene give very stable compounds. Ethylene can be displaced by a less volatile olefin, although the resulting compound may be less stable. Hydrogen will reduce the ethylene compound to platinum and ethane at atmospheric pressure and below 50°C. Concentrated hydrochloric acid and strong coordinating groups displace the olefin unchanged, but under controlled conditions a series of the type $(PtCl_2 \cdot uns \cdot A)$ can be made.

It has been generally assumed that these are platinous compounds. Ethylene platinous chloride can be made from platinous chloride and ethylene. Replacement of the olefin with other groups always gives a platinous compound. This is all indirect evidence however and does not really establish the valency of the platinum when coordinated to the olefin. Recently Hel'man has reported that in the electrometric titration of these compounds with permanganate in acid solution no oxidation was observed whereas platinous compounds were oxidized.

II. Structure

The structures which have been proposed can be divided into two classes, those in which the olefin rearranges and makes available a pair of electrons to the platinum, and those in which the platinum contributes a pair of electrons to the olefin. Dimer formation is explained by halogen bridges, olefin bridges and a platinum to platinum bond.

III. Discussion

A. Is the double bond broken?

The evidence is conflicting on this point. Previous workers have shown that in the case of cis and trans isomers generally only one form will react to give a crystalline compound and there is no transformation from one form to the other. Polymerization is only rarely observed.

This phase of the problem has been attacked in several ways.

1. Ultra-violet absorption spectra.

Due to its high resonance energy, trans-stilbene exhibits strong absorption in the ultra-violet at 2950 A. If the double bond were broken when the bond is made with platinum it might be expected that the absorption would decrease sharply due to the decrease in resonance energy. Absorption curves for trans-stilbene and trans-stilbene platinous chloride are almost identical. In the case of the styrene complex a new, strong peak appears in the region of the stilbene peak. However, pentene-1 platinous chloride has an absorption curve with very little character. No definite conclusions can be drawn from the ultra-violet work.

2. Infra-red absorption spectra.

Structural features in organic compounds give rise to characteristic absorption peaks in the infra-red. It should thus be possible to determine if the double bond is broken by the absence of the characteristic absorption peak of the double bond. It was found that in the case of styrene platinous chloride the double bond is completely gone. This observation is to be checked by studying compounds of cis- and trans- pentene-2, ethylene, cylclohexene, etc.

3. A study of cis- and trans- isomers

Infra-red studies on the complex compounds of cis- and trans- pentene-2 should prove very interesting. In addition to the determination of the existance of the double bond, some indication should be given as to whether there is free rotation if the double bond is broken or whether the structure is rigid. It seems quite probable that there is not free rotation since in some cases only one form will give a crystalline compound. For example, cis-pentene-2 platinous chloride is crystalline, the trans isomer is an oil.

Maleic and fumaric acids have also been used. Both react with potassium chloroplatinite but each in a different manner. Using the method of continuous variations and absorption in the visible it has been demonstrated that maleic acid reacts with potassium chloroplatinite in a ratio of 1-1. In the case of fumaric acid there is some reduction of the platinite to colloidal platinum which intefers with the measurement of the absorption spectrum.

However, working with the methyl and ethyl esters of these acids it is possible to isolate the complex compounds. A comparison of these products should be of value.

B. What is the nature of the bridging group?

The dimeric structure of $(PtCl_2 \cdot uns)_2$ has been explained by three different mechanisms already mentioned. If it is a halide bridge, it is to be expected that it would be broken upon the addition of 2 chloride ions to form $PtCl_3 \cdot uns^{-1}$, and the ion should be monomeric. This would not be true for an olefin bridge and the ion should remain a dimer. The molecular weight has never been determined. The same purpose will be served by determining the molecular weight of $(PtCl_2 \cdot C_2H_4 \cdot$quinoline). Boky has reported that the X-ray investigation of $(PtCl_2 \cdot NH_3 \cdot C_2H_4)$ shows that it is dimeric with a platinum to platinum bond and each platinum exhibiting a co-ordination number of 6. An actual physical determination of the molecular weight should settle this question.

References:

1. Keller, Coordination Compounds of Olefins with Metallic Salts, Chem. Reviews, 28, 229-267, (1941)

2. Ph.D. Thesis, A. L. Oppegard, University of Illinois, 1946

THE ELECTRODEPOSITION OF CHROMIUM

R. W. Parry June 11, 1946

I. The Commercial Chrome Plating Process

The commercial chrome plating bath is a solution 2 to 4 M in chromic acid (added as CrO_3) and .02 to .04 M in sulfate ion. The sulfate is essential to the process since chromium can not be plated from pure chromic acid. For most efficient operation the molar ratio of $CrO_4^=$ to $SO_4^=$ is maintained at 100 to 1.

II. Limitations of the Present Process

Although widely used, the chrome plating process has several limitations. 1) The current efficiency for chromium deposition runs about 5 to 20% of the theoretical value (based on Cr^{+6}) 2) Extremely high current densities ranging from 0.1 to 5.0 Amps/cm^2 are required. 3) Throwing power of the solution is poor. 4) The plate is porous, and 5) Chromium plated out on the cathode can not be replaced in the bath by anode corrosion.

III. Theories of Chrome Plating from $CrO_4^=$ or $Cr_2O_7^=$

Chromium deposition differs from normal electrodeposition in several particulars. 1) The metal to be reduced is carried in the anion 2) Deposition is not possible without an anion catalyst. (Deposits of chromium from pure $CrO_4^=$ have been reported at very low current density but in such cases the purity of the acid may be questioned since present day evidence indicates that rigorously pure $CrO_4^=$ will not plate) 3) The metal plated out can not be replaced satisfactorily by anode corrosion.

A. Theory of deposition now current in the literature.

It is assumed that $CrO_4^=$ (or $Cr_2O_7^=$ etc.) ions diffuse to the negative cathode against a potential gradient. At the cathode stepwise reduction of $CrO_4^= \longrightarrow Cr^{+++} \longrightarrow Cr^{++} \longrightarrow Cr$ is postulated; H^+ ions are used up simultaneously in the liberation of H_2. In this alkaline region immediately surrounding the cathode a basic film of chromic chromate forms and covers the cathode surface. It is assumed that the film thus formed is permeable to H^+ ions, but not to $CrO_4^=$ ions; thus $CrO_4^=$ ions are unable to reach the electrode and hydrogen is evolved. Sulfate ions supposedly act in some way, as yet undefined, to break the continuity of the film, and the reduction of chromium then proceeds. (Many investigators attribute the reduction of chromate to nascent hydrogen produced at the cathode.) The sulfate is also thought to to aid in stabilizing a layer of chromous ions on the metal surface.

The most obvious objections to this theory are 1) Although reduction is assumed to go through the Cr^{+3} state, Cr^{+3} solutions do not give a satisfactory plate. 2) The action of sulfate ions in making the film permeable is far from well defined. 3) A very pronounced film is visible over electrodes containing chloride catalyst but reduction is very efficient in this medium. 4) Reduction of $CrO_4^=$ by nascent hydrogen seems improbable. It is also noteworthy that the reverse reaction (oxidation of Cr^{+++} to $CrO_4^=$ is virtually impossible at a bright platinum anode but at a lead anode or in the presence of Pb^{++} the efficiency of oxidation approaches 100%. Here film formation is very improbable.

THE ELECTROMETALLURGY OF TANTALUM

J. W. Perry

June 21, 1944

I. The Commercial Chrome Plating Process

The commercial chrome plating bath is a solution of 2 to 4 M in chromic acid labeled as CrO_3, and .02 to .04 M in sulfate ion. The sulfate is essential to the process since pure chromic acid cannot be plated from pure chromic acid. For most efficient operation the "chromic-sulfate ratio" is 100. It is maintained at 100 to 1.

II. Limitations of the Present Process

Although widely used, the chrome plating process has several limitations. 1) The current efficiency for depositing metallic chrome ranges from 1 to 20% of the theoretical value (based on Cr^{+6}). 2) Extremely high current densities (several thousand amperes per dm^2) are required. 3) Increasing power of the solution is costly. 4) The plate is porous, and 5) Chromium plated out is not malleable and cannot be replaced in the bath by anode corrosion.

III. Theories of Chrome Plating from CrO_3 or $Cr_2O_7^{=}$

Chromium deposition differs from normal electrodeposition in several particulars. 1) The metal is deposited negatively from the anion. 2) Deposition is not possible without current. (Dipping of chromium from pure CrO_3 baths has reported for current density but is such as to cast the purity of the metal in question. Chromium plate prepared by evidence indicates that chromium plate CrO_3 will not plate) 3) The metal plated out can not be replaced satisfactorily by anode corrosion.

A. Theory of Deposition from Current in the Literature.

It is assumed that $CrO_4^{=}$ (or $Cr_2O_7^{=}$, etc.) ions diffuse to the negative anode against a potential gradient. At the cathode chromic reduction of $CrO_4^{=}$ ——→ Cr^{+3} ——→ Cr^{0} ——→ Cr is established if ions are used or alternatively in the intermediate Cr^{+2}. In this mechanism metals immediately succeeding the metals chrome form at anodic dissolve there not before the metals. It is assumed that the film thus formed is permeable to CrO_3, but not to CrO_4. Insoluble CrO_3 then may build up on the electrode and hydrogen is evolved. Films are made in this way, as yet undetected, to stop the continuity of film, and the reduction of chromic then proceeds. Insulating film is the production of chromic in chromic product or the cathode.) The matter is also thought to exist in establishing a layer of chromous ions at the metal surface.

The real driving mechanism this theory are 1) Activation is assumed to be through the Cr^{+2} state, 2) solution not plus a metallic chromic. 3) The action of metallic chromic the film permeable is the first well defined. 3) A very concentrated film is chromic over electrodes containing chromic layer but reduction is very efficient in this medium. 4) Inhibition of $CrO_4^{=}$ by chromic hydroxide stops increasing. The ex-

B. Chrome Plating from the Standpoint of Ionic Structure

A new theory of chromium deposition can be advanced from theoretical considerations based on the structure of $CrO_4^{=}$ ion. According to Rice (3) the chromate ion is in the form of a tetrahedron with the chromium atom in the center and the four oxygen atoms at the corners. The ion may be considered as formed from Cr^{++} and $4O^{-}$ groups. (Most stable structure from energy standpoint). The process of electrodeposition can now be broken down into a series of steps similar to those employed in the Born-Haber thermochemical cycle.

a) $CrO_4^{=}{}_{(aq)} \longrightarrow Cr^{++}{}_{(g)} + 4\,O^{-}{}_{(g)}$ $\Delta H = 957$ k cal

b) $Cr^{++}{}_{(g)} + 2e \longrightarrow Cr$ (solid metal) $\Delta H = -629$ "

c) $4\,O^{-}{}_{(g)} + 8H^{+}{}_{(aq)} + 4e \longrightarrow 4H_2O_{(l)}$ $\Delta H = -393$

$CrO_4^{=}{}_{(aq)} + 8H^{+}{}_{(aq)} + 6e \longrightarrow Cr_{(s)} + 4H_2O_{(l)}$ $\Delta H = -65$ k cal
E = about 0.2V

The energy of the first step of this process (a psuedo activation energy) would be 957 k cal/ mole. and the presence of hydrated Cr^{+++} in the solution would result from side reactions of hydration and reoxidation of Cr^{++} rather than from the formation of $Cr^{+++}{}_{(aq)}$ as an intermediate in the process.

The reduction of trivalent chromic ions may be subjected to similar thermochemical treatment.

a) $Cr(H_2O)_6^{+++} \longrightarrow Cr^{+++}{}_{(g)} + 6H_2O_{(l)}$ $\Delta H = 1320$ k cal

b) $Cr^{+++}{}_{(g)} + 3e \longrightarrow Cr$ (metal) $\Delta H = -1255$ k cal

---

$Cr(H_2O)_6^{+++} + 3e \longrightarrow Cr$ (metal) $\Delta H = +65.0$ k ca

In this case the ΔH valve for the initial reaction or the psuedo activation energy is 1320 k cal as compared to 957 for the reduction of chromate ion.

A similar consideration of chromous ion shows:

a) $Cr(H_2O)_4^{++} \longrightarrow Cr^{++}{}_{(g)} + 4H_2O_{(l)}$ $\Delta H = 672$ k cal

b) $Cr^{++}{}_{(g)} + 2e \longrightarrow Cr$ (metal $\Delta H = -629$

$Cr(H_2O)_4^{++} + 2e \longrightarrow Cr$(metal $+ 4H_2O_{(l)}$ $\Delta H = 43$ k cal

In this case the "activation energy" is only 672 k cal.

IV. Experimental Evidence

A number of plating trials in this laboratory and a large amount of data selected from the literature indicate a good qualitative correlation between ease of plating from $CrO_4^{=}$, Cr^{+++}, and Cr^{++} and the previously outlined activation energies.

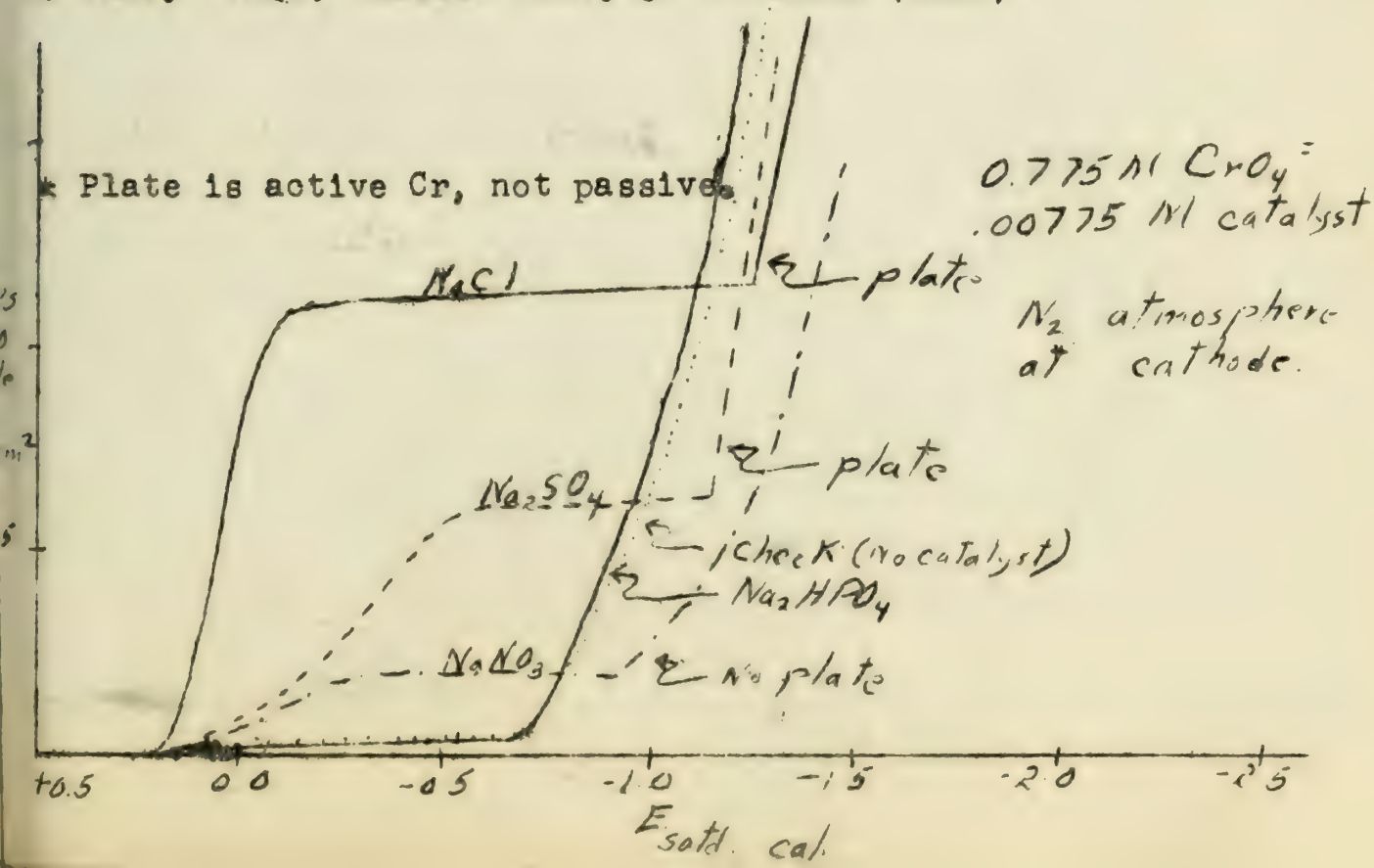
		ΔH
Cr^{++}	plates well,* efficiencies of 20-55% reported	627 K cal
$CrO_4^{=}$	plates well, efficiencies of 5-30% reported	957 K cal
Cr^{+++}	plates poorly, literature confused	1320 K cal

A more detailed study of the reduction of chromate solution in the presence of different catalysts is under way. The cathode potential during electrolysis is being followed in a special cell as a function of current density. Several curves are shown in Fig. 1. In the region A-B the solution darkens noticeably and $CrO_4^{=}$ is reduced to Cr^{+++}. As current density is increased the voltage suddenly jumps to a higher valve and hydrogen is evolved. If the potential jumps to a valve above 0.91 volts (H_2 std.) chromium is deposited along with hydrogen. If the valve is below this no chromium is deposited although hydrogen is evolved. It is interesting that this is close to the valve 0.86 V given by Latimer for the reaction $Cr^{++} + 2e \longrightarrow Cr$ (metal). These observations are difficult to haromonize with the film theory and with the theory of nascent hydrogen reduction.

An interesting but unexplained point is the varying efficiency of different anion catalysts. Without a catalyst hydrogen only is evolved and the chromate ion is not reduced. The relative efficiency of the catalysts in the reduction of $CrO_4^{=}$ to Cr^{+++} falls in the order $Cl^- > SO_4^{=} > NO_3^-$. $H_2PO_4^-$ is entirely without effect. The efficiency of the catalysts for metal deposition falls in the order $SO_4^{=} > Cl^-$. NO_3^- and $H_2PO_4^-$ were of no value. The nature of catalyst action is still under investigation.

References

1. Latimer- Oxidation Potentials- Prentice Hall, 1938
2. Bichowsky and Rossini-thermochemistry, Reinhold Rubl and Co. (1936)
3. Rice- Electronic Structure and Chemical Binding McGraw Hill Book Co. (1940)
4. Parry- Ph.D. Thesis- Univ. of Illinois (1946)



Inorganic Seminar

1946-47

TABLE OF CONTENTS

October 8, 1946

Clayton Callis

METAL DERIVATIVES OF AZO DYES

(Based on the master's degree thesis of Mr. Callis)

I. Introduction

The importance of the formation of metallic lakes of many azo dyes has been widely recognized for a number of years. Very little was known about the structure of these lakes until the last decade, even though they found wide use in the dyeing of fabrics.

The coordination of the dye molecules with the metal atoms greatly improves their fastness to washing and rubbing, as well as to light, and it has an important effect in modifying the shades. One of the most recent developments in connection with mordant dyes is the gradual tendency toward the use of the metallic lakes themselves as dyes, in preference to the process of mordant dyeing. These two processes are by no means equivalent. In many instances, the mordant process leads to the deposition in the fiber of more than one coloring lake, whereas the method of dyeing with the lake itself may be regarded as equivalent to dyeing with a single substance. Obviously, it would be of considerable advantage, in considering the mechanism of dyeing on various fibers, to know more about the structure and properties of these coloring lakes.

II. Previous Investigations

In 1908, Werner (1) pointed out that inner complex salts show considerable stability and that the color of such complexes depends upon the nature of the coordinated group. Since the metallic lakes of azo dyes exhibit unusual properties, many authors (2,3,4,5,6) were led to the assumption that there must exist some type of inner coordination of the metallic atom with one or both nitrogen atoms of the azo group.

In 1915, the first real attempt was made to determine the structure and composition of these lakes. A systematic study of the chromium lakes of azo dyes was made by Morgan (7), Morgan and Porter (8) and Morgan and Evens (9). The cobaltammine lakes of azo dyes were studied by Morgan and Main Smith (10), by Morgan and King (11) and by Morgan and Moss (12). These investigators, who used cobaltammines as sources of the cobalt lakes, concluded that the lakes contained one metallic atom to three dye residues bound in the inner sphere of coordination, but suggested that one hydroxyl group of a di-o-hydroxy dye was not implicated in the formation of the lakes.

Elkins and Hunter, (13) who in 1935 prepared nickel, copper and cobalt complexes from mono-ortho hydroxy azo dyes, point out that the formation of coordinated compounds is common to all o-hydroxy azo compounds.

The absorption spectra of several lakes were studied by Ernsberger and Brode (14) and by Haendler and Smith (15), who conclude that the color of the complex is apparently influenced less by the character of the substituent group in the organic portion than by the formation of the chelate bond.

The most important investigations of the structures of these metallic lakes were made by Drew in England. Copper lakes were studied by Drew and Landquist (16) in 1938, and by Beech and Drew (17) in 1940. Drew and Fairbairn (18) were interested in finding out what effect the extra valency of trivalent chromium, as compared with divalent copper, would have on the character of the lakes. Azo lakes of aluminum are described by Drew and Beech (17) and those of vanadium by Drew and Dunton (19).

Some general information that is known about the structure of these compounds is given below:

1. Coordination of the metal atom to the nitrogen is possible because the nitrogen possesses an unshared pair of electrons.

2. Either or both nitrogen atoms of the azo group can become coordinated. The stability is probably enhanced by a resonance process.

3. The formation of a stable three-membered ring including the metal atom and the two nitrogen atoms is not probable since the distance between the nitrogen atoms in azobenzene is 1.23 A^{o}, whereas the nitrogen-

nitrogen distance in $[Co(NH_3)_6]Cl_3$ is 2.8A°.

4. Coordination of the metal atom with azo nitrogen is possible only when the metal atom is affixed by covalent linkings (such as OH, CO_2H, or NH_2) which are in the o-position to the azo groups.

5. The stability is increased by the presence of two substituents of this kind in the o-o' positions, the lakes assuming fused ring forms.

The purpose of this investigation was to study the effect of the substituents in the o-positions on the valence and coordination number of the central metal atom and to extend the use of magnetic susceptibility measurements to the study of these metal derivatives.

II. Discussion of the experimental work (20).

1. In order to compare the effect of substituents in the oo' positions upon the nature of the complex formed, cobalt and nickel complexes of o-hydroxy, oo' dihydroxy, o-hydroxy-o'- carboxy, and o-hydroxy-o' - amino azo compounds were prepared. The ratio of metal atom to dye residue was determined by analysis, and the magnetic susceptibility of each complex was measured on a modified Curie-Cheveneau balance.

2. The data obtained indicate that the valence state of the cobalt is influenced by the nature of the dye molecule. Cobaltous complexes contain essentially ionic tetrahedral or octahedral bonds when the metal is coordinated thru oxygen or nitrogen atoms.

3. Nickel complexes of di-o-substituted dyes are tetrahedral. With mono-o-substituted dye either a tetrahedral or a planar structure is possible. Apparently the planar structure is more stable and is the preferred configuration.

BIBLIOGRAPHY

1. Werner, Ber., 43, 1062 (1908).
2. Baudisch, Z. angrew. Chem., 30, 133 (1917).
3. Morgan and Main Smith, J. Chem. Soc., 125, 1731 (1924).
4. Charrier and Peretta, Gazz. Chim. ital., 56, 865 (1926).
5. Crippa, Gazz. Chim. ital., 50, 20, (1937)
6. Cremonini, Gazz. Chim. ital., 58, 372 (1928).
7. Morgan, J. Soc. Dyers Colourists, 37, 43 (1921)
8. Morgan and Porter, J. Chem. Soc., 107, 645 (1915)
9. Morgan and Evens, J. Chem. Soc., 115, 1186 (1919)
10. Morgan and Main Smith, J. Chem. Soc., 119, 204 (1921); 121, 60, 286 (1922).
11. Morgan and King, J. Chem. Soc., 121, 1723 (1922).
12. Morgan and Moss, J. Chem. Soc., 121, 2857 (1922)
13. Elkins and Hunter, J. Chem. Soc., 1935, 1598.
14. Ernsberger and Brode, J. Org. Chem., 6, 331 (1941.)
15. Haendler and Smith, J. Am. Chem. Soc., 62, 1669 (1940)
16. Drew and Landquist, J. Chem. Soc., 1938, 292.
17. Beech and Drew, J. Chem. Soc., 1940, 608.
18. Drew and Fairbairn, J. Chem. Soc., 1939, 823.
19. Drew and Dunton, J. Chem. Soc., 1940, 1064.
20. Callis, M.S. Thesis, University of Illinois, Urbana, 1946

THE STRUCTURE OF THE SILICATES

October 15, 1946 G. K. Schweitzer

Introduction

Possibly the greatest contribution of crystal chemistry to science in general has been the systematic classification of the silicates. Attempts were first made at classification by postulating a series of theoretical acids thru the hydration of silica. Salts and mineral derivatives of a large number of these acids are known. Following is a table of these hypothetical silicic acids:

Table I-Silicic Acids

	Mono-	Di-	Tri-	Tetra-
	mH_2O-SiO_2	$mH_2O-2SiO_2$	$mH_2O-3SiO_2$	$mH_2O-4SiO_2$
Ortho-	H_4SiO_4	$H_6Si_2O_7$	$H_8Si_3O_{10}$	$H_{10}Si_4O_{13}$
Meta-	H_2SiO_3	$(H_2SiO_3)_2$	$(H_2SiO_3)_3$	$(H_2SiO_3)_4$
Meso-	-	$H_2Si_2O_5$	$H_4Si_3O_8$	$H_6Si_4O_{11}$
Para-	-	-	$H_2Si_3O_7$	$H_4Si_4O_{10}$
Tertero-	-	-	-	$H_2Si_4O_9$

This idea was widely held for some time; but since it is not completely in accord with the chemistry of the silicates, it has been abandoned.

There are several peculiarities making the study of the silicates very difficult. They are:

1. Silicates are insoluble in the majority of solvents.
2. Silicates have high melting points.
3. Silicates are chemically quite inert.
4. Silicates exhibit very complex structures, showing many Si:O ratios.
5. In silicates, the silicon may be replaced by many other ions: Fe^{++}, Fe^{+++}, Al^{+++}, Ca^{++}

Jakob (1) and Wahl (2) attempted to relate silicate structures to Werner's coordination theory, but met with failure because of the uncertainty that they were dealing with single molecules.

Bragg's Principles

An extensive X-ray study of the silicates by Bragg, his coworkers, and his contemporaries (3,4,5,6,7,8) suggested the following conclusions which led Bragg to a system of structure:

1. Oxygen ions, being the largest, form the skeleton of all silicate crystals.
2. Silicon <u>always</u> occurs in silicates surrounded tetrahedrally by four oxygen atoms.
3. The oxygen ions are shared by metallic elements; the silicon-oxygen tetrahedra may be connected with other groups thru these metallic ions.
4. The oxygens may be replaced by fluoride ions or hydroxide ions.
5. The other cations tend to symetrically distribute themselves throughout the crystal, giving the maximum electrical stability.
6. When two or more silicons share the same oxygen, the Si:O ratio varies accordingly.
7. The oxygen ions are always 1.62Å from the silicons; the oxygens themselves are separated by a distance of 2.6 to 2.8Å

Pauling's Principles

Pauling approached the subject of the silicate structure by assuming that each metallic ion (including Si^{++++}) lies at the center of a polyhedron whose corners are occupied by anions(9). He says that the cation-anion distance is determined by addition of the radii, and the coordination number is determined by the radius ratio. The radius ratio (10) may be defined as the ratio of the radius of the cation to that of the anion. The following tables show the utility of this idea:

Table II-Radius Ratios

Radius Ratio	Coord. No.	Configuration
up to .15	2	linear
.15 to .22	3	plane triangle
.22 to .41	4	tetrahedral
.41 to .73	4	plane square
.41 to .73	6	octahedral
.73 and up	8	cubic

Table III-Coord. No. of Ions in Oxides

Ion	Radius Ratio	Coord. No.	Bond Strength
B^{+++}	.20	3-4	1-3/4
Be^{++}	.25	4	1/2
Si^{++++}	.37	4	1
Al^{+++}	.41	4-6	3/4-1/2
Mg^{++}	.47	6	1/2-1/3
Zr^{++++}	.62	6-8	2/3-1/2

Pauling's ideas can be used quite successfully with the following limitations:

1. The anions must not be easily polarized.
2. The bonds must be essentially ionic.

Classification

From the observations of these two scientists, we see that we may consider the silicates as a close packed assembly of oxygen ions, with relatively small silicon and other cations fitted into the interstices so that each cation is coordinated with its required number of oxygen atoms. Silicon, having a coordination number of four, is invariably found at the center of a tetrahedral arrangement of oxygen atoms. The following classification is derived from the above principles and is in general usage today:

1. Self-contained groups
   a. SiO_4 single tetrahedra
      Examples: orthosilicates
      garnet (11)
      olivine (12) Mg_2SiO_4
   b. Si_2O_7 two tetrahedra sharing one oxygen corner
      Examples: thorveitite (13)
      hardystonite (14)
      melitite (15) $(Ca,Na)_2(Mg,Al)(Si,Al)_2O_7$
   c. Si_3O_9 three tetrahedra sharing corners with each other to form a closed ring
      Example: benitoite (16) $BaTiSi_3O_9$

2. Silicon-oxygen endless chains
   a. SiO_3 chains of SiO_4 tetrahedra each sharing two oxygens
      Example: diopside (17) $CaMg(SiO_3)_2$
   b. Si_4O_{11} double chains
      Example: tremolite (18) $Ca_2Mg_5(Si_4O_{11})(OH)_2$
3. Silicon-oxygen sheets
   Si_2O_5 groups
   sheets of SiO_4 tetrahedra each sharing three oxygen atoms
   Examples: micas; muscovite (19) $(OH)_2(K,Na)Al_2(Si_3AlO_{10})$
   chlorites; talc (20) $Mg_3Si_4O_{10}(OH)_2$
4. Silicon-oxygen three dimensional networks $(Si,Al)O_2$
   blocks of SiO_4 tetrahedra each sharing four oxygen atoms
   Examples: danburite (21) $CaB_2Si_2O_8$
   tridymite (22) SiO_2
   nephelite (23) $NaAlSiO_4$

Sharing of Corners, Edges, and Faces

In a stable coordinated structure, the electrical charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centers of the polyhedra of which it forms a corner. Thus in beryl, oxygen may be shared by two silicon ions ($1 + 1 = 2$) or by one silicon, one beryllium, and one aluminum ($1 + 1/2 + 1/2$). Other examples follow this idea quite coherently.

The presence of shared edges and faces in silicates decreases the stability. The loss of the stability is due to the close approach of the cations.

Sharing edge Si to Si is 0.58 x shared corner value
Sharing face Si to Si is 0.33 x shared corner value

Properties

An interesting group of minerals known as the zeolites form three dimensional structures. They undergo a process known as base exchange in which the metallic ions can be interchanged or the water removed and then readded without any apparent change in the structure. They are used quite effectively in water softening:

$$Na_2O\text{-}Al_2O_3\text{-}nSiO_2\text{-}mH_2O + CaSO_4 \longrightarrow CaO\text{-}Al_2O_3\text{-}nSiO_2\text{-}mH_2O + Na_2SO_4$$

general zeolite formula in H_2O — sol. in H_2O

Another base exchanger, similar to the zeolites, is permutite, an artificially produced alkali metal aluminum silicate of the general formula $2MO\text{-}Al_2O_3\text{-}3SiO_2\text{-}2H_2O$. If permutite is treated with water containing silver, calcium, magnesium, manganese, iron, and many other salts, these take the place of sodium.

The ultramarines form a series of sodium aluminum silicates containing sulfur compounds and possibly free sulfur. (24,25). Their structure is still not well characterized. It is known that they consist of an aluminosilicate skeleton in which exist alkali ions. The varied colors of the ultramarines are attributed to the presence of group VI elements (26,27,28). An example of this series is sodalite, [illegible] $Na_8Al_6Si_6O_{24}Cl_2$. Others contain S_x, Se_x, Te_x in place of the Cl.

Many silicates contain water, which can be driven off only at high temperatures showing that it is not water of crystallization. They are attacked by acids in many different ways. Some are readily decomposed by hydrochloric acid, even in the cold, the silicic acid separating as a jelly. Others are attacked slowly; still others not at all. In general, the more electropositive the metal in the silicate, the easier the decomposition. Hydrofluoric acid decomposes all silicates with the formation of gaseous SiF_4.

General References

1. Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry", Van Nostrand, New York, 1945, pp. 195-218.
2. Latimer and Hildebrand, "Reference Book of Inorganic Chemistry", MacMillan, New York, 1942, pp. 300-310.
3. Pauling, "Nature of the Chemical Bond", Cornell University Press, Ithica, New York, 1945, pp. 386-400.
4. Ephraim, "Inorganic Chemistry", Interscience Publishers, New York, 1946, pp. 825-831.
5. Stillwell, "Crystal Chemistry", McGraw-Hill, New York, 1938, pp. 286-306.

References

1. Jakob, Helv. Chim. Acta 3, 669 (1920).
2. Wahl, Z. Krist. 66, 173 (1927).
3. Bragg, Roy. Inst. Proc. 1927, 121.
4. Bragg, Trans. Faraday Soc. 25, 291 (1929).
5. Bragg, Z. Krist. 74, 273 (1930).
6. Bragg, "The Structure of the Silicates", 1932.
7. Bragg, "The Atomic Structure of Minerals", 1937.
8. Bragg and Bragg, "The Crystalline State", Vol. I, p. 131.
9. Pauling, J. Am. Chem. Soc. 51, 1010 (1929).
10. Goldschmidt, Ber. 60, 1263 (1927).
11. Menzer, Z. Krist. 69, 300 (1928).
12. Taylor and West, Proc. Roy. Soc. (London) A117, 132 (1928).
13. Zarhariasen, Z. Krist. 73, 1(1930).
14. Warren and Trantz, Z. Krist. 75, 525 (1930).
15. Warren, Z. Krist. 74, 131 (1930).
16. Zachariasen, Z. Krist. 74 139 (1930).
17. Warren and Bragg, Z. Krist. 69, 168 (1928).
18. Warren, Ind. Eng. Chem. 24, 419 (1932).
19. Pauling, Proc. Natl. Acad. Sci. 16, 123 (1920).
20. Gruner, Z. Krist. 66, 412 (1934).
21. Dunbar and Machatschki, Z. Krist. 76, 133 (1930).
22. Bannister, Mineralog. Mag. 22, 569 (1931).
23. Gunther-Schulze, Z. Electrochem. 27, 402 (1921).
24. Hoffmann, Z. anorg. allgem. Chem. 183, 37 (1929).
25. Jaeger, Trans. Faraday Soc. 25, 320 (1929).
26. Hofmann, Ber. 38, 2482 (1905).
27. Ostwald and Auerbach, Kolloid Z. 38, 336 (1926).
28. Ostwald, Z. anorg. Chem. 183, 37 (1929).

October 22, 1946

Robert A. Penneman

SOME APPLICATIONS OF ELECTRONICS TO EXPERIMENTAL CHEMISTRY

I. Filaments and Electron Emission

a) Pure tungsten 8.56 ma/cm^2/watt

b) Thoriated tungsten (1-2% Th) ca 100 ma/cm^2/watt

c) CaO-SrO coated filaments, low work function, ca 100 ma/cm^2/watt. Filaments are adversely affected by positive ion bombardment; on instruments having separate controls, it is important that filaments be allowed to heat before plate voltage is applied; also that plate voltage is turned off before filament voltage.

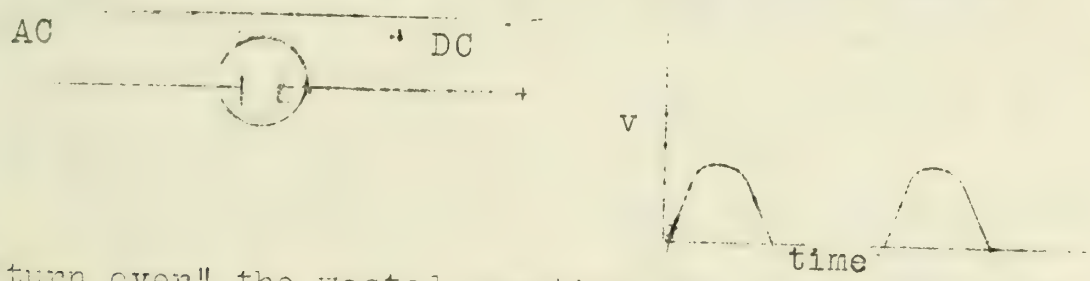
d) By using hollow cathodes, it is possible to heat them indirectly by using AC coils imbedded in a ceramic insulator.

e) In the later tube classification the numerical prefix denotes the approximate filament voltage, e.g. six volts (6.3v) 6K7, 6Q7; twelve volts, 12K7, 12Q7; twentyfive volts, 25A6; fifty volts, 50L6, hundred seventeen volts (can be operated directly from AC line) 117N7.

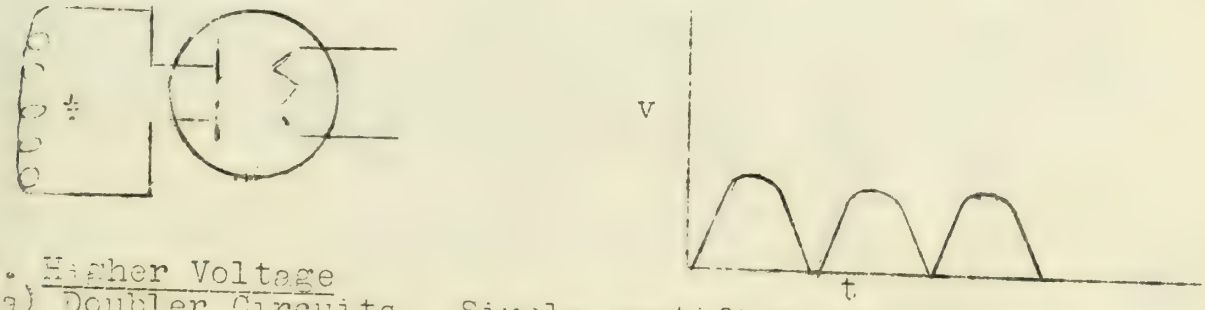
f) Common rectifiers have a five volt filament requiring 2-3 amps.

II. Rectification

Use of a diode "valve", conduction only on positive half cycle; thus converts AC into pulsating direct current.

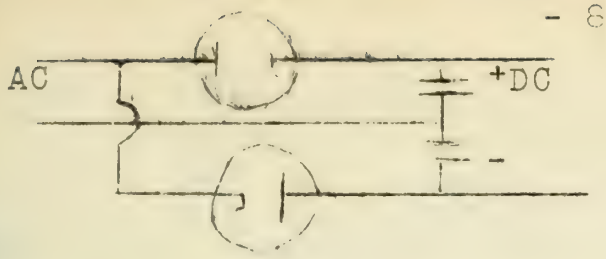


To "turn over" the wasted negative cycle and achieve full wave rectification is obviously more efficient and reduces the filtering problem.

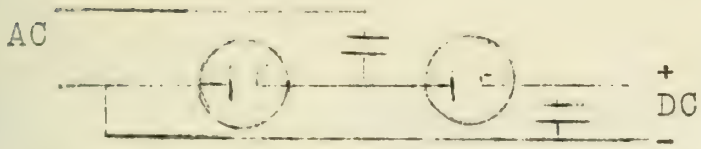


III. Higher Voltage

a) Doubler Circuits. Simple rectification produces, as a maximum, the highest input voltage; the following curcuits double this value (at zero current drain).



A disadvantage. Both sides of output are different from ground potential.



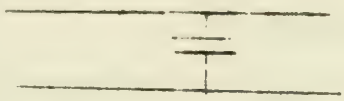
Half wave doubler. Common side can be at ground potential.

B) Higher voltages are conveniently obtained from a power transformer with AC input.

IV. Filtering

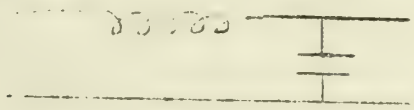
The pulsation present in the rectified AC cannot, in many cases, be used for plate or screen voltages. In radios it causes hum and can introduce error in measurements etc. To smooth out this "ripple" various circuits are appropriate.

a) Condenser



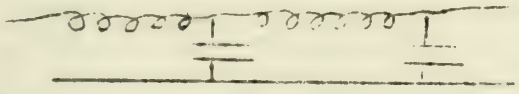
Voltage $=\sqrt{2}$ E where E is the RMS applied voltage. The condenser charges to peak applied voltage and helps to maintain that voltage during the ½ cycle until it is again charged. Thus the ripple is reduced.

b) Inductance and Capacitance



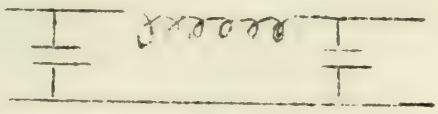
In this case, the voltage is partially smoothed out before reaching the condenser and filtering is improved.

c) Such sections can be multiplied until residual ripple is reduced to an amount that can be tolerated.



Choke input, with "π" section.

d) Condenser input.



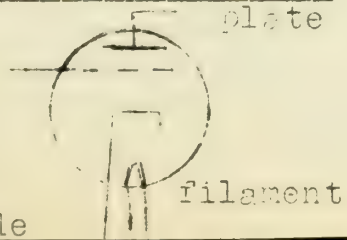
Condenser input allows higher voltages than choke input, for same applied voltage. Gas rectifiers are always followed by choke input to limit current.

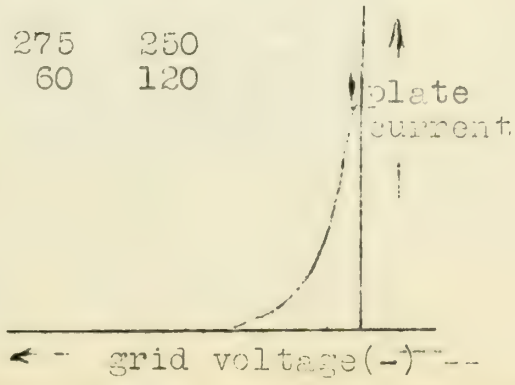
e) Obviously, with increasing current drain, the voltage at which it is available decreases: For a 5Y3, 350v RMS per plate, approximate values are:

Condenser input:	DC output, v:	450	390	340
	Current, ma :	20	60	120
Choke input:	DC output, v:	290	275	250
	current, ma :	20	60	120

V. Vacuum Tubes, On-Off Control

a) Triode



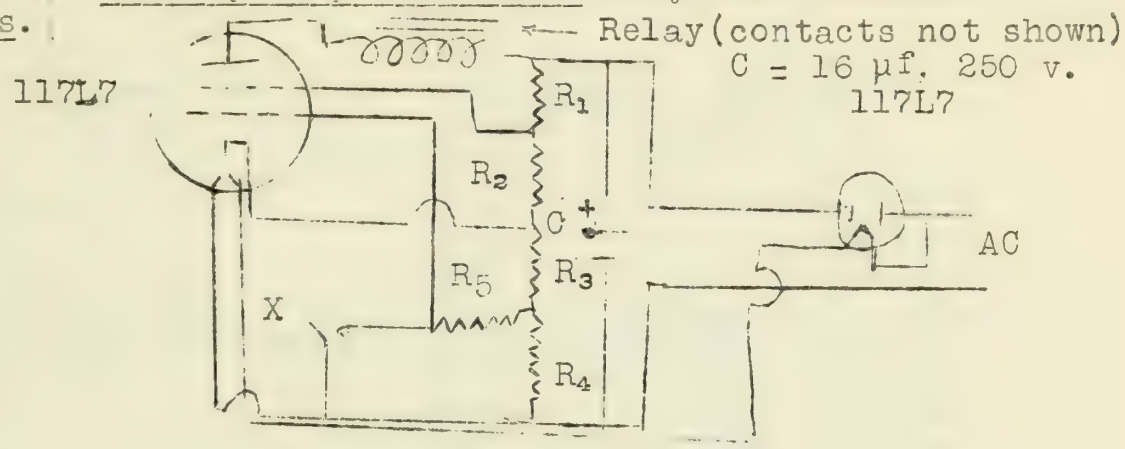


1) Cathode is taken as the zero reference point from which tube voltages are measured.

2) Grid bias is the negative voltage difference between the grid and cathode.

3) A tube is at "cutoff" when the grid voltage is sufficiently negative to reduce the plate current to a very low (zero) value.

b) Example of a simple relay circuit, using a 117L7. This tube contains a rectifier and amplifier in same envelope, but for clarity of presentation they will be shown as two tubes.



The relay is a Potter Bromfield relay of 1250 ohms resistance, and requires 20 ma to close.

An analysis of the steps in the calculation of the circuit is given to illustrate the method used.

When tube is conducting, 20 ma required for relay, plus 10 ma thru "bleeder" (arbitrary value) = 30 ma current drain. From manufacturer's charts of the tube characteristics, rectifier output at 30 ma drain (117 volt input) is 138 volts. Voltage drop in relay is 20/1000 x 1250 = 25 volts; to have plate more positive than screen voltage add 5 volts. E_1 = 25 + 5 = 30 v, ∴ R_1 = 30/10 x 1000 = 3000 ohms. Let E_2 (screen voltage) = 60 volts. (This is an arbitrary selection, but once chosen fixes the rest of the values) R_2 = 6000 ohms. Again from tube characteristics, a grid bias of -4 volts will allow the tube to pass 20 ma at a screen voltage of 60 volts. Remembering that both the bleeder current and the tube current pass through R_3, R_3 = 4/30 x 1000 = 133 ohms. By difference R_4 = 1467 ohms (1500).

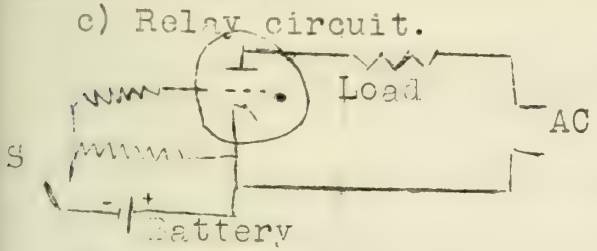
When the contacts at X are connected (by a Hg thermostat, for example) the tube ceases to conduct and the relay opens. This reduces the current drain and the voltage at the condenser will rise. Assume it rises to 150 volts; from the tube characteristics we see that the rectifier will furnish 15 ma at this voltage. The bleeder current is 150/10630 = 14.1 ma. Under these conditions, Plate voltage = 127 v, screen = 85 volts, grid =-23 v. A check of the tube characteristics shows that -23 volts will bias the tube to cutoff at a screen voltage of 85 volts. If this were not the case, the calculations would have to be repeated using slightly different values. The contact current = E_4/R_5 = $23/10^6$ = 23 µa (if R_5 is 1 megohm). Thus 23 µa at the contact points controls 20 ma plate current, which is turn operates the relay which can handle 5 amps. The "Sargent Zero Current Relay" utilizes a similar circuit but uses the relay to energize the coil of a 110 volt AC mercury relay which will handle 15 amps.

VI. Proportioning Control, Thyratrons

a) The thyratron is a triode filled with mercury, argon gas or some other inert gas at a pressure ca 1-2 cm. In this tube the grid serves only as a trigger. After the tube begins to conduct the grid has no further influence. Alternating current is usually applied to the anode, since the tube ceases to conduct 60 times each second, this allows the grid to regain control.

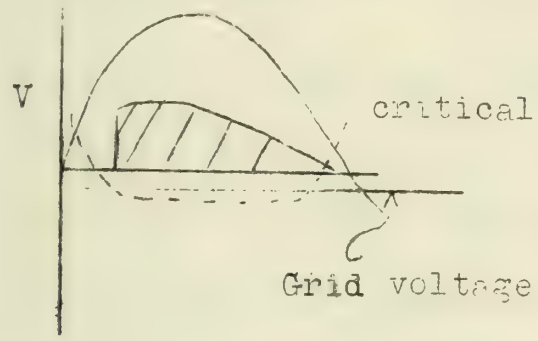
b) Of importance is their ability of carry currents of several amperes.

c) Relay circuit.

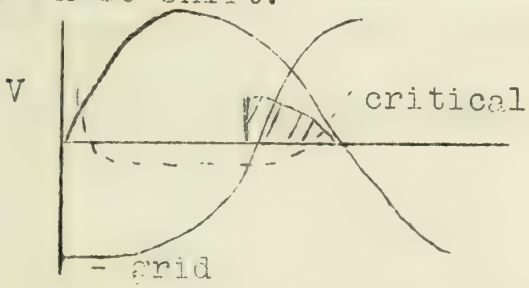


With S open, grid is at cathode potential and tube will conduct on every positive half cycle. With S closed, grid is negative and tube ceases to conduct.

d) The critical grid voltage which is necessary to allow conduction to begin varies with anode potential. If we choose the grid potential so it intersects the critical voltage curve, at that point the tube conducts (shaded area). The conduction can thus be varied over ½ the positive half cycle. This offers a poor method of control since the point of intersection cannot be closely controlled.

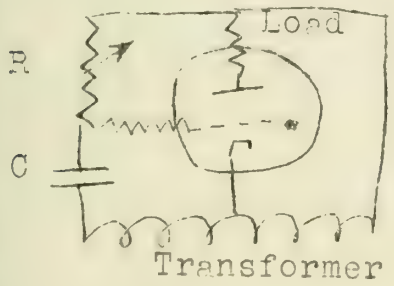


e) Phase shift.



In this method, the phase of the alternating grid voltage is varied and the tube current can be controlled over the complete positive half cycle.

The following circuit shows one method of accomplishing this.



If R = 0, grid and anode are positive and tube conducts. If R is large and C is large, grid is at opposite potential from anode and tube will not conduct. By adjusting C and R, conduction can be varied over this entire range. If C is constant, average anode current decreases as R increases. R can be a resistance thermometer (Pt) to control furnace temperature.

f) Thyratrons are useful to supply current to dual-field reversible motor. By direction of current, the motor can make adjustments to restore unbalance etc.

References

1. Strong, J., et.al. "Procedures in Experimental Physics", Prentice-Hall, Inc. N.Y. 1944, Chapter X.

2. [illegible], R.H., [illegible] Herman & M.E. Drop, "Experimental Electronics", Prentice-Hall, Inc. N.Y. 1944, Chapter 3,6

3. Livingston, [illegible] & H.H. Magoon, Electronics, April 1934

4. Tabol, R.M. & R.R. Hancox, Rev. Sci. Instruments, 5, 28 (1934)

5. Henney, K. "Electron Tubes in Industry", Second Edition, McGraw-Hill, N.Y., 1937

6. George, E.E. "Electronics," Aug. 1937; p. 19.

7. Beaver and Beaver, Ind. Eng. Chem. 15, 359, 1923

8. Ferguson, Van Lente and Hitchens, Ind. Eng. Chem. Anal. Ed., 4, 218, 1932.

9. Hawes, R.C., Ind. Eng. Chem. 11, 222, 1939.

10. Heisig and Gernes, Ind. Eng. Chem. 6, 155, 1934.

11. Huntress, E.H. and Hershberg, E.B. Ind. Eng. Chem. 5, 144, 1933.

12. Parks, Ind. Eng. Chem. 5, 356, 1933.

13. Semfass, E. J. Ind. Eng. Chem. 13, 262, 1941.

14. Waddel, H. H., and Salman, W., Ind. Eng. Chem. 12, 225, 1941.

15. Yee and Davis, Ind. Eng. Chem. 8, 477, 1933.

ELECTRODE REACTIONS IN LIQUID AMMONIA

Jack Nyman October 29, 1946

Only recently have the electrode potentials of metals in liquid ammonia been measured with a fair degree of accuracy. In 1907, Johnson and Wilsmore (1) measured the potentials of a series of metals by making use of the cell M|MX $Cd(NO_3)_2.4H_2O$(satd.)|Cd. Because hydrated cadmium nitrate was used in the reference electrode, and also the fact that no special precautions were taken to dry the ammonia, considerable doubt was thrown on these results. The values obtained by Johnson and Wilsmore are recorded below.

Electrode	E.M.F. (-35°C)
Ag/Ag NO_3 n/10	-0.963
Ag/Ag NO_3 n/100	-0.932
Ag/Ag I n/10	-0.885
Ag/Ag I n/100	-0.827
Hg/Hg I_2 n/10	-0.895
Hg/HgI_2 n/100	-0.867
Cu/$Cu(NO_3)_2.3H_2O$ n/1	-0.68
Cu/$Cu(NO_3)_2.3H_2O$ n/10	-0.70
Cu/$Cu(NO_3)_2.3H_2O$ n/100	-0.58
Pb/$Pb(NO_3)_2$ n/10	-0.515
Pb/$Pb(NO_3)_2$ n/100	-0.495
Ni/$Ni(NO_3)_2.6H_2O$ n/10	-0.500
Cd/$Cd(NO_3)_2.4H_2O$ n/10	+0.047
Cd/$Cd(NO_3)_2$ $4H_2O$ n/100	+0.086
Zn/Zn $(NO_3)_2.6H_2O$ n/10	+.353
Zn/$Zn(NO_3)_2.6H_2O$ n/100	+.376
$NH_4(Hg)_x$/NH_4NO_3 n/10	+.91
Mg/MgI_2 n/100	+1.26
Ca/$Ca(NO_3)_2.4H_2O$ n/10	+1.48
Na/$NaNO_3$ n/10	+1.56
Na/NaCl n/10	+1.58
K/KI n/10	+1.59

Johnson and Wilsmore also attempted to relate the electrode potentials of metals in liquid ammonia to those in water by use of a cell of the type

$$\underset{(-35°C)}{Cd|Cd(NO_3)_2.4H_2O\ (saturated)|NH_4OH|Hg_2Cl_2 + KCl\ N/10\ (aq)|Hg}\ \ 25°C$$

Measurement of potentials of cells of the latter type are without meaning because of the fact that there is a liquid junction potential and a temperature gradient in the NH_4OH bridge which will cause indeterminate effects in the e.m.f.

Since 1935, Pleskov and Monosson (2,3,4,5,6) have carried out very careful measurements in anhydrous liquid ammonia at -50°C. Their results are recorded in the following table, on the basis of the $Rb = Rb^+ + e^-$ electrode being taken as 0. At various points in the progress of their work, they used $Pb|Pb^{++}$ and $Hg|Hg^{++}$ as reference electrodes. The Rb electrode was finally selected

because of the fact that rubidium amalgam gave a very steady and reproducable potential in liquid ammonia. A table of electrode potentials in anhydrous by hydrazine as determined by Pleskov (6) is also listed for comparison.

Element	$E_{N_2H_4}$	E_{NH_3}	E_{H_2O}
$Li \mid Li^+$	+0.19	+0.31	+0.09
$K \mid K^+$	+0.01	+0.05	+0.01
$Cs \mid Cs^+$	---	+0.02	---
$Rb \mid Rb^+$	0	0	0
$Ca \mid Ca^{++}$	-0.10	-0.29	-0.16
$Na \mid Na^+$	-0.18	-0.08	-0.22
$N_2 \mid NH_2^-$	---	-0.57	---
$Zn \mid Zn^{++}$	-1.60	-1.40	-2.17
$Cd \mid Cd^{++}$	-1.91	-1.73	-2.53
$H_2 \mid NH_4^+$	-2.01	-1.93	-2.93
$Cu \mid Cu^+$	-2.23	-2.34	-3.45
$Cu \mid Cu^{++}$	----	-2.36	-3.28
$Pb \mid Pb^{++}$	-2.36	-2.25	-2.80
$O_2 \mid OH^-$	---	---	-3.33
$Hg \mid Hg^{+2}$	---	-2.68	-3.79
$Ag \mid Ag^+$	-2.78	-2.76	-3.74
$I^- \mid I_2$	---	-3.38	-3.51
$Br^- \mid Br_2$	---	-3.76	-4.01
$Cl^- \mid Cl_2$	---	-3.96	-4.29

Several different methods were employed to obtain these values. For the less active metals, cells of the type $M \mid M(NO_3)_x$ 0.1N$\mid KNO_3$ (saturated)$\mid Pb(NO_3)_2$ 0.1 N $\mid$ Pb were set up and the measurements made directly using $Pb \mid Pb(NO_3)_2$ 0.1 N as a reference electrode. In the case of the more active metals, it was necessary to measure the potential of an amalgam of known concentration, against the Pb half cell and then calculate the standard potential of the metal. This calculation can readily be made if the potential difference between the amalgam and the metal is known. It was fortunate that for the alkali metals this potential difference had been previously measured.

The e.m.f. of the hydrogen electrode was measured against a lead electrode by Pleskov and Monosson (7) and found to be reversible. These authors (8) also used concentration cells involving hydrogen electrodes to calculate the activity coefficients of ammonium nitrate at various concentrations.

Pleskov (9) found that the nitrogen electrode was irreversible, but that a value could be obtained for the electrolytic evolution of nitrogen. The evolution of nitrogen is shifted toward the positive side in liquid ammonia in contrast to oxygen evolution in water because of the small ΔF of formation of ammonia. The theoretical decomposition potential of liquid ammonia amounts to 0.082 V at -50°C.

Elliott and Yost (10) found the e.m.f. of the cell at 25°C. $Zn(Hg)\ (s)\ |\ ZnCl_2.6NH_3(s)/NH_4Cl\ (a_2 = 1)/TlCl(s)\ Tl(Hg)s$ to be .9016 volts, and if the Zn and Tl were present as pure metals, 0.8293 volts. Garner, Green, and Yost (11) found that the e.m.f. of the cell $Zn(s)\ ZnCl_2.6NH_3, NH_4Cl, (a_2 = 1)\ CdCl_2.6NH_3)Cd(s)$ at 25°C. is 0.3605 volts. Ritchey and Hunt (12) using values of the activity coefficients of ammonium chloride which they determined at 25°C, and the experimental measurements of Yost and coworkers, calculated the e.m.f. of the following half cells on the basis of hydrogen = 0.

		E°_{298}
$Tl(s) + Cl^- \longrightarrow TlCl(s) + e^-$		0.0371
$Zn(s) + 2Cl^- + 6NH_3(l) \longrightarrow$	$ZnCl_2.6NH_3(s) + 2e^-$	0.8664
$Cd(s) + 2Cl^- + 6NH_3\ (l)$	$CdCl_2.6NH_3(s) + 2e^-$	0.5059

It was noticed by Palmaer (13) that blue streaks appeared near the cathode when a liquid ammonia solution of tetramethyl ammonium chloride was electrolyzed. Schulbach (14) observed a similar phenomenon with several tetraalkyl ammonium ions. He also reported that the substitution of hydrogen for an alkyl group decreased the stability of the ions.

Forbes and Norton (15) measured the oxidation potentials of several NR_4 groups in the following manner. They first electrolyzed a solution of NR_4I in liquid ammonia at -75° between two platinum electrodes and obtained at the cathode a blue solution of NR_4 radicals. Then using another platinum electrode in the NR_4 solution and a Silver-sat. silver nitrate electrode, separated by a ground glass joint, they measured the potential of the $NR_4 \longrightarrow NR_4^+$ oxidation.

Radical	E.M.F. obs. (average)	E.M.F. connected to .005 M
$N(CH_3)_4$	2.593	2.585
$N(C_2H_5)_4$	2.597	2.590
$N(C_3H_7)_4$	2.602	2.596
$N(C_4H_9)_4$	2.585	2.578
$N(C_2H_5)_2(C_4H_9)_2$	2.597	2.595
$N(C_2H_5)C_4H_9)_3$	2.601	2.599
$N(CH_3)_3(C_4H_9)$	2.592	2.590

$N(C_2H_5)_3(C_4H_9)$	2.600	2.595
$N(C_3H_7)_3(C_4H_9)$	2.583	2.578
$N(C_4H_9)_3(CH_3)$	2.596	2.595
Li	2.606	---
Na	2.603	2.594
K	2.601	---

The potentials of the alkali metals was measured against several NR_4 groups by use of the cell

Pt|M , MI|NR_4 , NR_4I|Pt. It was found that all of the oxidation potentials of these radicals and of the alkali metals were within 25 millivolts of each other, and that the Nernst equation was not valid for these solutions. That is, a change in concentration of the metal, salt, or radical did not effect the electrode potential markedly.

It is apparent that the formation of this blue solution involves a transfer of an electron from the cathode to the solvent, or to the NR_4^+ ion to form an NR_4 radical. In view of the work of Kraus (16,17) it appears that the best representation would be NR_4^+ ions and solvated electrons. Kraus found that when a current is passed through solutions of alkali metals in liquid ammonia, the concentration of the metal ion is increased at the cathode, as indicated by a deepening of the blue color. At the anode, the reverse phenomenon occurs; the conc. of M^+ decreases and the blue color in the immediate region disappears. There is no evidence for an electrode process other than the transfer of an electron from the solvent to the electrode. Conductance measurements indicate that the solution is composed of sodium ions and solvated electrons.

On this basis it would appear that the reduction potential of the NR_4^+ groups and the alkali metal ions should be dependent only on the electron concentration of the solution and should obey the equation $E = E^\circ - \frac{RT}{nF} \ln (C \text{ electron})$.

BIBLIOGRAPHY

(1) Johnson, F.M.G., and Wilsmore, N.T.M., Trans. Faradi Soc. 3, 70, (1907)
(2) Pleskov and Monosson, Acta Physico Chim. 2, 615 (1935).
(3) Pleskov and Monosson, Acta Physico Chim. 2, 628 (1935).
(4) Pleskov, Acta Physico Chim. 13, 659 (1940).
(5) Pleskov, Acta Physico Chim. 13, 662 (1940).
(6) Pleskov, Acta Physico Chim. 21, 235 (1946).
(7) Pleskov and Monosson, Acta Physico Chim. 1, 871, (1935).
(8) Pleskov and Monosson, Acta Physico Chim. 1, 715, (1935).
(9) Pleskov, Acta Physico Chim. 20, 578, (1945).
(10) Elliott and Yost, J. Am. Chem. Soc. 56, 1057, 2797, (1934).
(11) Garner, Green, and Yost, J. Am. Chem. Soc. 57, 2055, (1935).
(12) Ritchey and Hunt, J. Phys. Chem. 43, 414, (1939).
(13) Palmaer, Z Electro Chem. 8, 729, (1902).
(14) Schulbach, Ber. 53, 1689, (1920).
(15) Forbes and Norton, J. Am. Chem. Soc. 48, 2278, (1926).
(16) Kraus, C.A., J. Am. Chem. Soc. 30, 1323, (1908).
(17) Kraus, C.A. J. Am. Chem. Soc. 36, 864, (1914)

INORGANIC CHROMATOGRAPHY

Matheson, A. R. November 5, 1946

I. Introduction

Inorganic chromatography is used herein as the term applied to the process whereby solutions of inorganic substances are passed through a column containing a finely divided solid material, the "adsorbent", upon which solid the inorganic substances are retained to a greater or lesser degree. The remainder of the solution passes on through the column. The formation of zones of various colors upon the body of the solid material is called a "chromatogram". In some cases it is necessary to "develop" the column after the original solution has passed through the column in order to produce a visible banding. Development is usually brought about by various chemical means. Once the zones have been developed the inorganic substances present may be identified by color or position in the series, or both; the column may be physically extruded and divided at the various zonal boundaries; or, by using a suitable liquid the zones can be made to move ("elution") through the column and the "eluate" caught fractionally and analyzed for components.

II. Historical

Tswett (25) in 1906 made the first chromatographic separation when he poured a petroleum ether extract of driet leaf material through a column of precipitated chalk and obtained a separation of materials into several colored zones. The method was little used until 1931 when an examination of carotene and xanthophyll materials indicated its usefulness.

The first reference to the use of chromatography for inorganic substances was made by Lange and Nagel (18) in 1936, who from theoretical considerations, proposed that rare earths should be capable of being separated by chromatographic adsorption. Schwab and his co-workers (20-24) made note of this proposal but did not work with the rare earths. Instead in a preliminary communication Schwab and Jockers (20) reported that the separation of inorganic materials from solution, using alumina as an adsorbent, was very useful and that the resulting chromatograms exhibited bands or zones containing the various components of the solution.

Schwab and his co-workers have contributed most of the basic work on inorganic chromatography. In recent years the method has been expanded by various means and the development is continuing today.

III. Apparatus

The apparatus varies widely from a simple glass tube with a constriction near one end, glass wool, rubber stopper and a suction flask, to the complex apparatus developed by Tiselius (4) whereby the properties of the eluate may be physically evaluated immediately after passing through the adsorbent. Columns range in size from a few millimeters to several inches in diameter and a few centimeters to several feet in length. Strain (6) and Zechmeister (7) have many illustrations of special apparatus.

IV. Materials

Materials used may be divided into three general classes, i.e. adsorbents, solvents and eluants, and developers.

A. Adsorbents

For inorganic chromatography activated alumina, silica gel, 8-hydroxyquinoline, violuric acid, and some oxime derivatives have been used. The preparation of the adsorbents is an industry within itself. The nature of the adsorbent can be varied to fit the problem. A good adsorbent should be granular, reasonably even in particle size, inert (unless it is desired to form a compound with the solute), and insoluble in the liquids used.

B. Solvents and eluants

The solvent being used depends upon the nature of the substances being investigated and the nature of the adsorbent itself. A list of solvents of increasing polarity ranging from petroleum ether to water solution of acids and bases is used as a guide. Adsorption is greatest from non-polar solvents. Eluants are in most cases the more polar solvents of the series. The complete series is listed in Strain, and Zechmeister. Water is the most frequently used solvent in inorganic chromatography with acids as eluants.

C. Developers

The development of the zones is important, particularly in inorganic chromatography. Addition of a more polar solvent often widens the bands and moves them down the column and sometimes serves as a development process. With a comparatively weak adsorption from water acids cannot be used to develop the column so some substance is added to the water which will react with the adsorbed material and give a colored product. Solutions of H_2S, $(NH_4)_2S$, $NaOH$, $K_4Fe(CN)_6$ have been used as developers.

V. Applications

Most of the inorganic application of chromatography has been carried out in Europe, although Bishop (8) has suggested the use of inorganic chromatography for undergraduate work in the separation of various inorganic ions.

Schwab and his co-workers have carried out many experiments on inorganic adsorption and as a result of their work they came to the conclusion that the adsorption process is one of ion exchange wherein the cation in question is exchanged upon the column of alumina for a sodium ion. The sodium ion is contained in the alumina as a basic sodium aluminate. For anions to be exchanged there must be bound to the alumina an anion which the anion in solution may displace. An alumina column treated with acid produces a column whereupon certain anions may be exchanged. Hesse (3) divides chromatography into two parts, (a) true adsorption in which only surface forces between the solution and solid are considered, and (b) exchange adsorption where ions in solution displace ions from the column of adsorbent. Jacobs and Tompkins (17) consider inorganic adsorption as part true adsorption and part ion exchange.

They believe that inorganic ions would be better adsorbed from purely cation exchange materials.

A. Cation exchange

Cations may be exchanged for a sodium ion or an alumina column, or exchanged for a H ion in a compound such as 8-hydroxy quinoline to form metal quinolate.

Schwab and Jockers (20) investigated the adsorption of various inorganic ions upon alumina both from aqueous solutions and from solutions containing tartrate ion. The use of ammonia causes a definite alteration in the sequence of adsorption. From an aqueous solution the sequence of ions from top to bottom of the column is as follows:

$$As^{+++}\ Sb^{+++},\ Bi^{+++},\ \begin{matrix} Cr^{+++} \\ Fe^{+++} \\ Hg^{++} \end{matrix},\ UO_2^{++},\ Pb^{++},\ Cu^{++},\ Ag^{+},\ Zn^{++},\ \begin{matrix} Co^{++} \\ Ni^{++} \\ Cd^{++} \\ Fe^{++} \end{matrix},\ Tl^{+},\ Mn^{++}.$$

With ammonia the series becomes $Co^{++}, Zn^{++}, \begin{matrix} Cd^{++} \\ Cu^{++} \end{matrix}, Ni^{++}, Ag^{+}$.

Erlenmeyer and Dahn (14) used 8-hydroxy quinoline as the adsorbent and obtained a colored series as follows: VO_3^{-}, grey-black; WO_4^{--}, yellow; Cu^{++}, green; Bi^{+++}, yellow; Ni^{++}, green; Co^{++}, reddish; Zn^{++}, yellow; Fe^{+++}, black; UO_2^{++}, red-orange. In an other experiment (15) violuric acid was used as the adsorbent and a series of zones of the alkali and alkaline earth metals complexes was formed. A micro-quantative determination of Na and K was made using violuric acid and 5-oxo-4-oximino-3-pheny-isoxazoline in the same column as adsorbents (16).

Clarke (1) reports that Venturello and Agliardi in 1940, used an alumina column to separate a number of inorganic ions, apparently similarily to the work of Schwab and others.

The first investigator to carry out Lange and Nagel's suggestion for the separation of the rare earths appears to be Erämetsä (11). A sample containing the rare earths and yttrium was dissolved and the solution (neutral) was passed through a column of alumina. The Y was less adsorbed than the rare earths and some shifts in composition were noted, although no pure separation was claimed. A tartrate solution was also used and resulted in a lesser amount of Y being adsorbed than before and a larger amount of the yttrium earths being adsorbed Yttrium does not appear to follow the true lanthanides as far as basicity behavior is concerned in these experiments. A second experiment (12) was carried out with similar results to that above. Citrate complexing caused some changes in the sequences, and carbonate complexing permitted a better separation of the cerium group for the yttrium group. Silica gel was used for an adsorbent in one column. Croates (9) has also studied the chromatographic adsorption of the rare earths. It is reported that a preferential adsorption of Ce^{++++} with respect to La^{+++} and the formation of two zones was brought about, but the details are unknown since the original article has not been available.

Erämetsä (13) in an unsuccessful attempt to find a complexing agent for the rare earths used diphenylthiocarbazone ("Dithizone") to prepare dithizonates of several metals (antimony, tin, nickel, manganese, copper, etc.,). The dithizonates were in a $CHCl_3$ solution and this solution was poured through an alumina column resulting in quite sharp banding. CCl_4 solutions were also employed.

B. Anion exchange

Schwab and Dattler (21) separated some of the more common anions such as OH^-, PO_4^{---}, F^-, $Fe(CN)_6^{---}$, CrO_4^{--} etc., but found it was not possible to separate all anions because of the difficulty in forming colored compounds.

VI. Theory

Wilson (26) has proposed a theory for chromatography which has been applied largely to organic processes. DeVault (10) has modified this to a certain extent. Meyers (19), and Jacobs and Tompkins (17) have made some application of the theory to inorganic processes.

General references

1. Alexander, J., Colloid Chemistry, Reinhold Publishing Corp., New York,(1944),Vol. V. 457-491 (Beverly Clarke- author).
2. Bottger, W., Physikalische Methoden der Analytischen Chemie, Akad. Verlag-gesellschaft, Leipzig, (1939), pp. 1-7, 30-73.
3. Hesse, G., Adsorption methoden im Chemischen Laboratorium, Gruyter and Co., Berlin, (1943), pp. 29-33; 107-113.
4. Kraemer, E. O., Advances in Colloid Chemistry, Interscience Publishing Inc., New York, (1942, pp. 81-98; 333; 341
5. MacDougall, F. H., Physical Chemistry. The MacMillan Co., New York, (1943), pp. 681-3.
6. Strain, H. H., Chromatographic Adsorption Analysis,(1942),pp.1-82
7. Zechmeister, L, and Cholnoky, L, Principles and Practices of Chromatography, (Trans. Bacharach, A.L. and Robinson, F.A.) John Wiley and Sons,Inc., New York, (1941), pp. 1-88; 304-24.

Special references

8. Bishop,J., J. Chem. Educ., 22, 524 (1945)
9. Croatto, K., C.A., 37, 2680 (1943; Ricerca Sci., 12, 157 (1941).
10. DeVault, D., J. Am. Chem. Soc. 65 532 (1943).
11. Erämetsä, O., Bull. Comm. Geol. Finlande, 14, 36 (1941).
12. _____, Sahama, Th., and Kanula, V., Ann. Acad. Sci. Fennica,A, 57, No. 3, 5 (1941).
13. Erämetsä, O., Suomen Kemistlehti, 16B, 13 (1943).
14. Erlenmeyer, H. and Dahn, H., Helv. Chim. Acta. 22, 1369 (1939).
15. _____, and Schoenauer, W., ibid., 24, 878 (1941).
16. _____, and Schmidlin, J., ibid, 24, 1213 (1941).
17. Jacobs, P.W. and Tompkins, F. C., C.A. 39 5156, 5157 (1945; Trans. Faradya Soc., 41, 388-94; 395-400; 400-5 (1945).
18. Lange, E. and Nagel, K., Zeit. fur Elektrochem., 42, 210 (1936).
19. Meyers, R. J., Eastes, J.W., and Urquhart, D., Ind. Eng. Chem. 33, 12[illegible] (1941).

20. Schwab, G.M., and Jockers, K., Zeit. fur Elektrochemie, 43 610 (1937); Naturwissenschaften, 25, 44 (1937); Angew. Chemie, 50, 546 (1937).
21. _____, and Dattler, G., ibid., 50, 691 (1937).
22. _____, _____, ibid., 51, 709 (1938).
23. _____, and Ghosh, A.N., ibid, 52, 666 (1939).
24. _____, _____, ibid., 53, 39 (1940).
25. Tswett, M., Ber. deut. botan. Ges., 24, 384 (1906).
26. Wilson, J.N., J. Am. Chem. Soc., 62, 1583 (1940).

ION EXCHANGE

Starr, Donald November 12, 1946

I. Introduction

Ion exchange has been described as the reversible interchange of ions between a liquid phase and a solid, involving no radical change of the solid (29). The existence of such a phenomenon was first noticed by Way in 1845 (31) when he passed an ammonium chloride solution through a column of soil and found calcium ions, in place of ammonium ions, in the effluent. Thompson (26) is also given credit for the discovery.

Other materials, zeolites in particular, were found to posess this base-exchanging property. Technical application of these exchangers to the softening of water dates back about forty years. Many varied uses have been found for the process since the discovery of the ion exchange capacity of organic resins (1).

II. Types of Exchangers

A. Cation

Many natural materials, clays, zeolites, glauconites for examples, have ability to exchange ions. Some treated, naturally occurring substances have been used in treating hard water. Synthetic "zeolites" have been produced from sodium silicate and sodium aluminate. (29) Carbonaceous exchangers are those produced by the action of SO_3 on coal (3). The phenol-formaldehyde type of resins are widely used at present (5).

B. Anion exchange absorbents

Some inorganic exchangers have been mentioned but their use is limited (12). (29) The most useful materials for anion exchange or acid absorption are the basic resins (13).

III. Ion Exchange Reactions

These reactions are reversible and represented thus:

$$Ca^{++} + 2\,(Na^{+}Ex^{-}) \rightleftharpoons 2Na^{+} + (Ca^{++}\,Ex_2^{-})$$

where Ex represents the cation exchanger.
In this example the exchanger operates on the sodium cycle. Operation according to the hydrogen cycle is analogous. Regeneration of the exchanger is possible because of the reversibility of the reactions.

Acid adsorption is represented as follows:

$$(R_3N) + HCl \longrightarrow (R_3N{\cdot}H^{+}\,Cl^{-})$$

or:

$$(R_3NH^{+}\,OH^{-}) + HCl \longrightarrow (R_3N{\cdot}H^{+}Cl^{-}) + H_2O$$

where R_3N represents an anion exchanger.
After an anion is attached to the exchanger it can be exchanged for another anion:

$$SO_4^{=} + 2\,(R_3NH^{+}Cl^{-}) \rightleftharpoons \left[(R_3NH^{+})_2SO_4^{=}\right] + 2Cl^{-}$$

Thus a combination of hydrogen cycle exchange followed

by acid adsorption will result in complete removal of all electrolytes from solution. This is referred to as deionization or demineralization.

Several workers (2) (4) (6) (12) (15) (30) have examined the reactions of exchangers in a static system. They brought weighed quantities of dried materials into contact with various solutions and determined the extent of exchange after equilibrium had been established. Likewise work has been done with exchangers in dynamic systems by allowing solutions to flow through columns of exchange materials (12) (13) (25). Generally ion exchangers are utilized in industry under such conditions. Using this method, the usable, or "break-through", capacity can be determined. This capacity is the quantity of ion which is exchanged up to the point where it first appears to a detectable amount in the effluent.

Ion exchange reactions have been shown to obey the mass action law or closely approach such conditions (2) (7) (12). Most of the exchange occurs in a few minutes, but true equilibrium is attained slowly (15) (16) (27). The reaction rate of anion exchange is much slower than that of cation exchange (13). Temperature has been shown to have little effect on the reaction rate (16) or equilibrium (6).

Nachod and Wood showed the influence of anions on cation exchange (16). Salts in the form of the acetate, formate or bicarbonate were exchanged to a greater degree than the corresponding chloride, nitrate, or sulfate. Correlation has been seen between the size of the hydrated ion and the extent of exchange (16) (29). In general, the larger the hydrated ion, the smaller is the amount of the exchange. Increased charge upon an ion produces more exchange. (16)

The pH is known to effect the exchange. Nelson and Walton (17) explain the increased exchange of calcium ions in solution for hydrogen ions in an exchanger at higher pH values, by citing the existence of the very weakly acidic groups in the resin, which will exchange in alkaline solution but not in acid solution.

IV. Applications

Ion exchangers have been used for a number of varied purposes. Water conditioning has been the largest field for technical application of ion exchangers. Water comparable to distilled water can be produced in this manner at lower cost.

Myers (11) and Sussman and Mindler (23) have written reviews on the uses of ion exchange materials in industry. These applications include removal of ionic impurities from sugar solutions, (32) removal of formic acid from formaldehyde, and removal of objectionable ions found in crude petroleum.

As well as removing undersirable ions, valuable materials may be recovered from solution. Exchromium, gold, iron, molybdenum, palladium, platinum and vanadium, in the form of anions (22). Copper ions have been recovered from cuprammonium rayon waste liquors. Alkaloids (21) and tartrates (9) have been obtained in pure form in this manner.

Electrolytes can be separated or fractionated by this process. This has been applied to amino acid separation (28), to rare earth separation by Pearce and Russell (18), and to fractionation of lithium isotopes by Taylor and Urey (24). Separations for analytical purposes have been used by Frizzell (8) and Samuelson (20).

In industry ion exchange has the disadvantages of any batch process, in that the exchanger bed must be regenerated at intervals. Semi-continuous operation is obtained by the use of several columns, one or more of which may operate while the others are being regenerated.

Due to the capactities of the exchangers, the process is limited to solutions of relatively low concentration. With increasingly higher concentrations of ions, the volume of solution which can be treated decreases until the volume of exchanger required is larger than the volume of solution used. This is seen in the demineralization of sea water to produce drinking water. It has been estimated that two liters of ordinary exchangers would be required to desalt one liter of sea water. During the war, however, a high capacity ion exchanger, with silver as the exchangeable ion, was used by the Armed Forces for this purpose (23).

Thus, ion exchange is definitely out of the question for some processes, but the versatility of the process can be seen. It has been suggested that because of its general application, it should be mentioned with distillation and filtration as a unit process of chemical industry. (28)

References

1. Adams, B.A. & Holmes, E.L., J. Ind. Chem. Soc. 54, 1T (1935)
2. Akeroyd, E.I. & Broughton, G., J.Phys.Chem., 42, 343 (1938)
3. Applebaum, S.B. & Riley, R., Ind.Eng.Chem. 30, 80 (1938)
4. Austerweil, G.V., J.Soc.Chem.Ind., 53, 185T (1934)
5. Bauman, W.C., Ind.Eng.Chem., 38, 46 (1946)
6. Ferguson, J.B., Musgrove, J.R., and Patton, J.R. Can.J.Res.B. 14, 243 (1936)
7. Furnas, C.C., and Beaton, R.H., Ind.Eng.Chem. 33, 1500 (1941)
8. Frizzedl, L.D., Ind.Eng.Chem., Anal.Ed., 16, 615 (1944)
9. Matchett, J.R., Legault, R.R., Nimmo, C.C., & Notter, G.K., Ind.Eng.Chem. 36, 851 (1944)
10. Morrison, W.S., Monthly Rev.Am. Electroplaters Soc, 30, 702 (1943) C.A., 37, 6195 (1943)
11. Myers, R.J., "Synthetic Resin Ion Exchangers", in E.O. Kramer "Advances in Colloid Science", Interscience Publishers Inc., New York, 1942
12. Myers, R.J., Eastes, J.W. & Myers, F.J. Ind.Eng.Chem., 33, 697 (1941
14. Nachod, F.C. & Sussman, S., J.Chem. Education, 21, 56 (1944)
15. Nachod, F.C., & Wood, W., J.Am.Chem.Soc., 66, 1380 (1940)
16. Nachod, F.C., and Wood, W., J.Am.Chem.Soc., 67, 629 (1945)
17. Nelson, R, and Walton, H.F., J.Phys.Chem., 48, 406 (1944)
18. Pearce, D.W. & Russell, R.G., J.Am.Chem.Soc., 65, 595 (1943)
19. Ryznar, J.W., Ind.Eng.Chem., 36, 821 (1944)
20. Samuelson, O., Z. anal.chem., 116, 328 (1939)
21. Sussman, S., Nachod, F.C., and Wood, W., Chem.Ind., 57, 455, 549 (1945)
22. Sussman, S., Nachod, F.C., & Wood, W. Ind.Eng.Chem., 37, 618 (1945)
23. Sussman, S., & Mindler, A.B. Chem.Md., 56, 789 (1945)
13. Myers, R.J., Eastes, J.W. & Urquhart, J.D. Ind.Eng.Chem. 33, 1270 (1941)

24. Taylor, T.I., & Urey, H.C., J.Chem.Phys, 6, 429 (1938)
25. Thomas, H.C., J.Am.Chem.Soc., 66, 1664 (1944)
26. Thompson, J., J.Roy.Agr.Soc.Engl., 11, 68 (1850); 13, 123 (1852)
27. Tiger, H.L., & Sussman, S., Ind.Eng.Chem. 35, 186 (1943)
28. Walton, H.F., J.Chem.Education, 23, 454 (1946)
29. Walton, H.F., J.Franklin Inst. 232, 318 (1941)
30. Walton, H.F., J.Phys. Chem., 47, 371 (1943)
31. Way, J.T., J.Roy.Agr.Soc.Engl. 11, 313 (1850)
32. Weitz, F.W., Sugar, 38, No.1, 26 (1943)

VALENCE STATES OF IRON

Weaver, Eugene November 12, 1946

I. Introduction

Iron, which is found to be the fourth element in abundance on the earth's surface and the backbone of the so called "steel age", is also important as a component of chemical compounds. We are familiar with the ferrous and ferric compounds and need to become more familiar with the higher valences of iron.

II. Iron's position in the Periodic Table.

Iron is found in the eighth group and is a transitional element in the first long period. These elements are grouped in threes, which are called triads because of their similarity. The similarity between iron, cobalt and nickel is due to the fact that electrons are filling an underlying shell.

Similarities may be expected among iron, ruthenium and osmium since the 3d, 4d, 5d levels are being filled in the respective elements. Both ruthenium and osmium form tetra-oxides so a similar compound might be expected for iron.

Sidgwick (7) points out that according to the covalency rule the highest valence for iron is six so it would not be expected to form a tetra-oxide.

III. Suggested valence states of iron.

Using ruthenium and osmium as examples we can expect to find the valence states which are listed in the table. They are the valences which have attracted the most attention of investigators.

Valence	+2	+3	+4	+6	+8
Oxide	FeO	Fe_2O_3	FeO_2?	$\{FeO_3\}$	$\{FeO_4\}$
Acid properties		Increasing →			
Acid	$\{H_2FeO_2\}$	$HFeO_2$	$\{H_2FeO_3\}$	$\{H_2FeO_4\}$	$\{H_2FeO_5\}$
Name	Hypoferrous acid	ferrous acid	perferrous acid	ferric acid	perferric acid
Representive compound	$\{Na_2FeO_2\}$	$NaFeO_2$	$BaFeO_3$	$BaFeO_4$	$\{K_2FeO_5\}$
Name	Sodium hypoferrite	Sodium ferrite	Barium perferrite	Barium ferrate	Potassium perferrate

Oxidation potentials (3)

$$Fe \xrightarrow{.44} Fe^{++} \xrightarrow{-.77} Fe^{+++} \xrightarrow{-1.9} FeO_4^{=}$$

$$Fe \xrightarrow{.88} FeO_2^{=} \xrightarrow{.68} FeO_2^{-}$$

$$Fe \xrightarrow{.88} Fe(OH)_2 \xrightarrow{.56} Fe(OH)_3 \xrightarrow{-0.9} FeO_4^{=}$$

Equilibrium potentials (15)

$$Fe \xrightarrow{-.86} FeO_3^{=} \xrightarrow{-.69} FeO_2^{-} \xrightarrow{0.55} FeO_4^{=}$$

The acid properties of the oxides increase with the valence of the iron. The acids are named in the same manner as the oxygen acids of chlorine were named. The compounds listed have all been reported as having been prepared.

IV. Experimental work reported in the Literature.

The literature has many references to the formation of salts of the acidic iron oxides. These references go back to the early 18th century. The compounds will be discussed in order of their valence states.

Iron also forms several interesting types of compounds of lower valence.

Finely divided iron reacts with carbon monoxide to form the pentacarbonyl $Fe(CO)_5$ in which the valence of iron is zero according to our usual idea of valence.

$Fe(NO)_2I$ has been prepared from $Fe(CO)_4I_2$ and NO. In the former the apparent valence of iron is one.

A. Hypoferrites

Grube and Gmelin (15) conducted an experiment in which they dissolved an activated iron anode in 40% sodium hydroxide solution. They plotted the anode potential against current density and obtained a curve containing two inflections. They took this to mean the formation of sodium hypoferrite and sodium ferrate.

B. Ferrites

Grube and Gmelin found that ferrites could be prepared by anodic oxidation of alkaline ferrous solutions or cathodic reduction of sodium ferrate if platinum electrodes were used. Ferrites may also be prepared by fusing ferric oxide and sodium carbonate at red heat.

Bernard and Chandron (8) found that they could prepare the ferrites of cobalt, nickel, magnesium and manganese by heating the oxides of these metals with magnetite at 800° in a vacuum. Calcium, strontium and barium did not react, apparently because their size was not near enough that of the ferrous ion.

Songuet (23) observed that ferrites of cobalt, nickel, copper and zinc could be prepared by heating together the precipitated hydroxides. Calcium, magnesium, and zinc ferrites are well defined crystalline compounds.

C. Perferrites

Pellini and Meneghini (20) observed that an alcoholic solution of ferrous chloride reacted much differently with hydrogen peroxide than ferric chloride and hydrogen peroxide which showed very little reaction. These men assumed that the product of the oxidation of the ferrous salt was iron dioxide.

Moser and Borch (18) heated to dryness a solution of ferric nitrate and strontium nitrate. The residue was heated in a current of oxygen and strontium perferrite was obtained.

The perferrites are stable below 640°. Above this temperature they evolve oxygen and the iron is reduced to the ferric state.

The perferrites are fairly stable in alkaline solution.

Bray and Gorin (10) have suggested that FeO^{++} ions exist in equilibrium with the ferric ion.

Another example of tetra-valent iron is found in FeS_2 which is obtained when Fe_2S_3 is treated with H_2S (13).

D. Penta-valent Iron

Manchot and Wilhelms (17) studied the reaction of hydrogen peroxide and potassium iodide in the presence of ferrous salts. Calculations based on the amount of iodine liberated seem to indicate the formation of FeI_5. Selwood (6) mentions a similar compound, NH_4FeF_6, in which the iron would be penta-valent.

E. Ferrates

Grube and Gmelin (14) expanded on their work mentioned earlier and built a cell in which they used superimposed alternating current on direct current. They got good yields of sodium ferrate in that manner.

Losana (16) prepared potassium ferrate by two general methods:

(a) Iron powder was thrown into fused potassium nitrate.

(b) A rapid current of chlorine gas is passed thru a suspension of ferric hydroxide in concentrated potassium hydroxide solution.

The silver, barium, calcium, lead zinc, nickel and cobalt salts may be dried without decomposition.

On heating, a stepwise decomposition occurs.

$$Ba\,FeO_4 \xrightarrow{123^\circ} Ba\,FeO_3 \xrightarrow{144^\circ} BaO + Fe_2O_3$$

F. Perferrates

Goralevich (11) reported that he prepared a green compound when he fused together ferric oxide, potassium hydroxide and an excess of potassium nitrate. He said that the green compound was a perferrate.

Petroo and Ormont (21) reinvestigated Goralevich's work and came to the conclusion that the green compound was a manganese compound rather than an iron compound.

Kulgina and coworkers found that by first purifing the ferric oxide they got no green compound.

G. Summary.

It can be pointed out that the vertical relationship in the periodic table is as important as the triad relationship.

The stability of the compounds containing higher valent states increases with atomic number.

The acids of valences 3, 4 and 6 form stable compounds.

The ferrate ion is a powerful oxidizing agent.

References

1. Abegg, "Handbuch der anorg. chemie" Vol. 13, part 3 2nd half B 290, B 427
2. Caven and Lander "Systematic Inorganic Chem." Blackie and Son, London, 1931, page 367
3. Latimer and Hildebrand, "Reference Books of Inorganic Chemistry" Macmillan, New York 1940, p. 390
4. Latimer "Oxidation Potentials", Prentice-Hall New York 1938, p. 208
5. Mellor "Inorganic and Theoretical Chemistry" Longmans New York, Vol. 13, p 494, 905
6. Selwood "Magnetochemistry" Interscience Publishers Inc. New York 1943 p. 155
7. Sidgwick "Electronic Theory of Valency" p. 295 Oxford University Press, 1929
8. Benard, J. and Chandron, Georges Compt. rend. 204 766-8 (1937)
9. deBoca, Armando Anales farm bioqum 6, 65-9 (1935)
10. Bray, W.C. and Gorin M.H., J.Am.Chem.Soc. 54, 2124 (1932)
11. Gorelevich, D.K. Phys.Chem.Soc. 58, 1129-58 (1928); C.A. 22, 1294 (1928)
12. Gorgoraishvili, Kulgina and Zoyagintsev; J.Gen.Chem. (USSR) 9, 1961-6 (1939); C.A. 34 5011 (1940)
13. Griffith and Morcom J.Chem.Soc. 1945 786-90
14. Grube, G. and Gmelin, H. Z. Elektrochem 26 153-61 (1920)
15. Grube, G. and Gmelin, H. ibid 26 459-71 (1920)
16. Losana, L. Grazz.Chim ital 55 468-97 (1925); C.A. 20 156 (1926)
17. Manchot, W. and Wilhelms, M. Ber 34 2479 (1901); Liebigs Ann 325 105 (1902)
18. Möser, L. and Borch, H. Ber 42 4279 (1909)
19. Ormont Acta physicochim URSS 11 1911-16 (1939); C.A. 34 4622 (1940)
20. Pellini, G. and Meneghini D. Zeit. anorg. chem. 62 203 (1909)
21. Petrov, B. and Ormont, B. J. Phys Chem. (USSR) 8 665-76 (1936); C.A. 31 2113 (1937)
22. Petrov, B. and Ormont, B. J. Gen. Chem. (USSR), 7, 1690-4 (1937) C.A. 31, 8329 (1937)
23. Sonnet, Jackqueline, Compt. rend. 213 577-9 (1941)

COMPOUNDS OF METHYL SULFIDE WITH INORGANIC SUBSTANCES

November 19, 1946 William G. Britton

Introduction

Sulfur has the property of exhibiting the greatest variety of valence forms of any of the elements occurring in organic compounds (1). This paper is a review of some chemical and physical properties of methyl sulfide which makes readily available information needed to predict the course of hitherto unknown reactions of this compound.

Description of Compounds

1. With halogens

Under anhydrous conditions sulfides react with the halogens (except flourine) to form dihalide addition products which might be considered as having a structure similar to that of sulfonium salts.

$$RSR + X_2 \longrightarrow [R\overset{X}{\overset{\uparrow}{S}}R]^+ X^- .$$

The formation of dihalides occurs with great ease when methyl or methylene groups are adjacent to sulfur; in fact, the reaction with bromine takes place so readily that it has been used as a quantitative method for the determination of sulfides (2). The compound

$[Me\overset{Br^+}{\overset{\uparrow}{S}}Me]^+ Br^-$ is a yellow crystalline solid (3).

II. With platinum salts

When excess methyl sulfide is added to aqueous $PtCl_4$, (4)

A. $PtCl_3.2Me_2S$ is formed
B. $PtCl_4.2Me_2S$ is formed on recrystallizing
C. $PtCl_2.2Me_2S$ is formed after evaporation in a vacuum desiccator.

Compound A appears to have one methyl sulfide molecule not coordinated. When $PtBr_4$ acts on Me_2SBr_2 (5)

D. $PtBr_4.2Me_2S$, an orange red material, is formed on standing in alcohol.
E. $PtBr_6^{--}(Me_2SBr^+)_2$, a dark red material, is formed when D is washed with alcohol.

Compound E appears to have a bromine atom on one side of the sulfur, the other side of which is coordinated with the platinum.

More complex compounds are formed (6) when Me_2S reacts with K_2PtBr_4 and HBr yielding

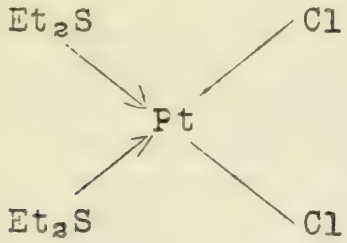
F. $[Pt(Me_2S)_4]PtBr_4$.

$PtCl_2.2Me_2S + [Pt_4NH_3]Cl_2$ on shaking with water form (7)

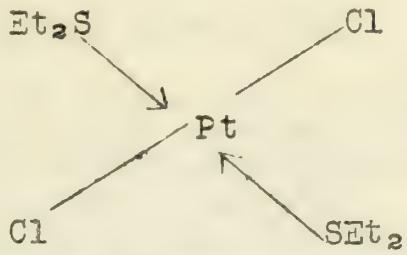
G. $[Pt_4NH_3]PtCl_4 + [Pt_4Me_2S]Cl_2. + [Pt(NH_3)_4][PtCl_4]$

The ammonia complex has the form of Magnus' salt $[Pt_4NH_3]PtCl_4$.

A few years ago three chemists brought severe criticism on themselves (1). It has long been known that the following two modifications exist for $PtCl_2 \cdot (Et_2S)_2$.

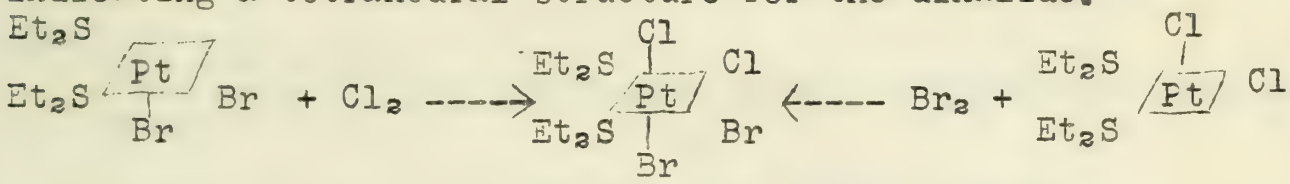


α Werner

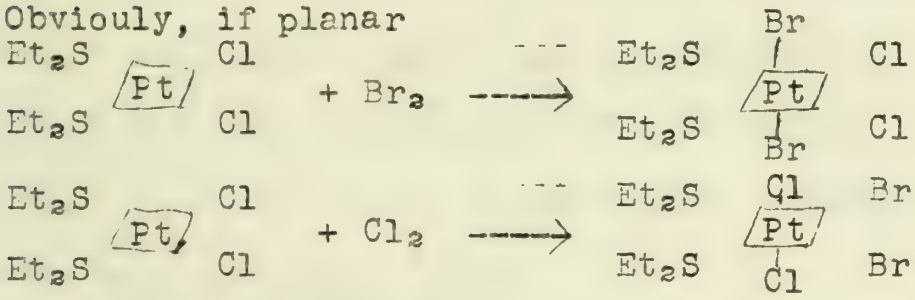


β Werner

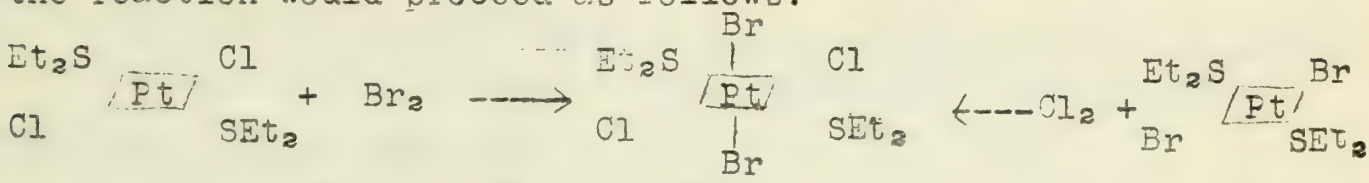
Angell, Drew and Wardlaw found that the reaction of the α dichloride with bromine and the α dibromide with chlorine yields one and the same dibromo dichloride. They interpreted this as indicating a tetrahedral structure for the dihalide.



Obviouly, if planar



As would be expected, the theorists were severely criticized, so they decided that the α forms were really the β forms and the reaction would proceed as follows:



III. <u>With mercury salts</u>

A. General reaction

Organic sulfides combine with mercury salts according to the type formula

$$R_2S + HgI_2 = R\text{-}\underset{R}{S} \rightarrow HgI_2$$

Mercuric chloride is used in separating sulfides from petroleum distillates. Treatment with hydrogen sulfide regenerates the sulfides (2).

B. With mercuric halides

Loir discovered the ability of organic sulfides to form compounds with certain heavy metal salts and assigned the formula $(CH_3)_2S \cdot HgCl_2$ to the mercuric chloride compound. Phillips reported the formula of $3HgCl_2 \cdot 2(CH_3)_2S$ (8). There is a possibility that the product is a molecular compound made up of $Me_2S \cdot HgCl_2 + Me_2S \cdot 2HgCl_2$ (8).

Smiles reports the existence of the mercuric iodide compound Me_2SHgI_2 (8).

C. With mercurous nitrate

$$R_2S + Hg_2(NO_3)_2 \longrightarrow (R_2S)_2Hg(NO_3)_2 + Hg.$$

Mercury is oxidized to a higher valence state (8).

D. Effect of solvent

In some cases the solvent is an important factor. Methyl sulfide does not react with mercurous chloride unless water is present but reacts readily with mercurous acetate or sulfate in the absence of water.

E. Comparison of methyl sulfide with other sulfides in reactions with mercury salts.

All organic sulfides react with aqueous $Hg_2(NO_3)_2$ or with aqueous or anhydrous Hg_2SO_4. Only methyl sulfide reacts with Hg_2Cl_2 and then only in the presence of water. Only methyl sulfide reacts with mercurous acetate in the absence of water. Other sulfides require water.

IV. With gold salts

The general type reaction of alkyl sulfides with gold salts is stepwise (9).

$$AuCl_3 + R_2S \longrightarrow AuCl_3 \cdot R_2S \text{ (a yellow complex)}$$

$$AuCl_3 \cdot R_2S + R_2S + H_2O \longrightarrow AuCl \cdot R_2S + R_2SO + 2HCl \text{ (colorless)}$$

The compound Me_2SBr_2 acts on $AuCl_3$

$$Me_2SBr_2 + AuCl_3 \xrightarrow[EtOH]{} Me_2SBr^+ \quad AuCl_3Br^-$$

V. With palladium salts

Solid products that are obtained by reaction with palladous chloride are used for the identification of sulfides (2).

VI. With trimethyl aluminum

$Me_2S \cdot AlMe_3$ exists. Methyl ether coordinates more strongly toward trimethyl aluminum than does methyl sulfide (10).

VII. With iridium chloride

$$IrCl_4 + Me_2S \xrightarrow[\substack{EtOH \\ \text{(heat)}}]{} Ir_2Cl_5 \cdot 4Me_2S$$

The same reaction at room temperature gives $IrCl_3 \cdot 2Me_2S$ (11)

VIII. With alkyl halides

$$RSR + RX \longrightarrow R\text{-}\overset{\overset{R}{|}}{S}\text{-}R^+ \; X^-$$

The reaction is slow at room temperature and proceeds more readily on heating (2).

IX. Summary

The sulfides form sulfonium-like compounds with halogens and alkyl halides, coordination compounds with salts of heavy metals as the result of the donor activity of sulfur; and as would be expected, some of the more complex compounds aren't adaptable to the Werner scheme but probably form "hydrate like" structures.

Physical Properties

It is interesting to compare some of the physical properties of methyl sulfide with those of methyl ether and also to investigate some physical methods of examining methyl sulfide and see how the properties of the very reactive sulfur atom manifest themselves.

A. General observations

	Melting Point	Boiling Point	Solubility in Water (1
Methyl ether - colorless gas	-138.5°	-23.65°	3700cc/10
Methyl sulfide - colorless liquid -	83.2°	37.5°	insoluble

The low molecular weight sulfides have odors which, though disagreeable, are not so objectionable as those of the mercaptans (2). Experiments carried out on fasting female rats in a gas chamber show that dimethyl sulfide irritates the mucous membrane, paralyzes the voluntary muscles, and finally the respiratory muscles. A concentration of 5% is fatal in 15 minutes. Dimethyl disulfide is more irritating while of/methyl mercaptan is less (13).

B. Raman Spectrum

A beam of mono-chromatic light has its frequency altered when scattered by a liquid in a way which depends on the nature of the scattering molecules. The change in frequency is dependent upon a characteristic frequency of the molecule. A mechanical analogy with weights and springs agrees remarkably with actual data. The Raman spectrum gives an indication of the numbers of atoms in a molecule, the masses of the atoms, the strength of the chemical bonds, and degree of ionization (14). As yet, the Raman specturm for methyl sulfide has not been developed to the extent that unknown information can be obtained from it (15)

C. Barrier potential

Until recent years it was supposed that rotation of a methyl group about the C-C bond was quite free, but the view of restricted rotation is now generally accepted. Absence of isomers does not conflict with this idea because the magnitude of the barrier potential is 3 k. calories and it would have to be of the magnitude of 20 k. calories to allow isomers at ordinary temperatures (16). The cause of this restriction to rotation is mutual repulsion of the hydrogen atoms.

The barrier potential must be considered in calculating any thermodynamic property of a substance at any temperature (16).

The barrier potential of methyl sulfide is smaller than for methyl ether and larger than for methyl mercaptan (17). This is to be expected because the oxygen atom is smaller than the sulfur and therefore in ether the methyl groups are closer together than in methyl sulfide.

It can be shown that this hindering of rotation is mainly due to the proximity of the methyl groups rather than to the type of atom to which they are attached (18).

D. Bond angle

C-S-C angle is 100 -110°	(18)
H-S-H angle is 92°	(16)
H-O-H angle is 105°	(16)

E. Dipole moment

The moment of sulfides is higher than that of ethers, but contrary to what would be expected, the moment of sulfides is higher than that of mercaptans even though the moment for ethers is lower than for alcohols (19).

F. Ionization potential (20)

Decreasing potential

$$Me_2O > Et_2O > H_2S > EtSH > Me_2S > Et_2S$$

G. Summary

Methyl sulfide differs from methyl ether in its boiling point, melting point, and solubility in water as would be expected from the difference in molecular weight. The odor and toxicity are representative of sulfur compounds. The Raman spectum offers little data; the barrier potential reflects the size of the sulfur atom; the bond angle shows no striking peculiarity but the dipole moments an interesting relation between ethers, alcohols, mercaptans and sulfides is found.

Preparation and Purification

The general method of preparation for symmetrical sulfides is shown by the type reaction (2)

$$RX + K_2S \longrightarrow RSR + 2KX.$$

Mercaptans and water are the main impurities and removal can be affected by refluxing with copper and sodium, fractionating, allowing to stand in vacuo to expel non-condensable gases, and fractionating again. By this method an impurity of only .007 mole % remains (17).

Summary

Methyl sulfide compounds with inorganic substances are listed and seem to be divided into sulfonium-like compounds, coordination compounds, and more complex compounds difficult to classify. Some physical properties of methyl sulfide are discussed and interesting relationships between physical properties and related compounds are shown. Finally methods of preparation and purification are reviewed.

References

1. Gibson, D. T., "Significant studies in the Organic Chemistry of Sulfur", Chem. Reviews 14, 431 (1934)
2. Gilman, H., "Organic Chemistry", Wiley and Sons, 1943.
3. Hantzsik, A, and Hibbert H., "Addition Products of Tri-Alkyl Phosphines, Arsines, and Stibines", Ber., 40, 1508-19 (1907)
4. Prafulla, C. R. and Purna, C. M., "Action of Bases on Complex Compounds Derived from Organic Thio Compounds and PlatinicChloride". J. of Ind. Chem. Soc. 6, 885-91 (1929).
5. Pietro, Spinoglio and DeGasperi, Mario, "Structure of Ki-halogenodialkyl Sulfides and of Dihalogenodialkyl Selenides and Their Complexes with Auric Chloride and Platinum Tetra bromide", Gazz. chim. ital. 67, 318-24 (1937).
6. Chugaev, L. and Fraenkel, D., "Complex Compounds of Platinum Bromide and Organic Sulfides", Compt. rend. 154, 33-5 (1912)

7. Tshugaev, L. and Suffotin, V., "Isomeric Platinum Compounds of Organic Sulfides", Ber., 43, 1200-5 (1910).
8. Faragher, W. F., Merrell, J. C., and Camay, S., "Interaction of Alkyl Sulfides and Salts of Mercury", J. Am Chem. Soc. 51, 2774-81 (1929).
9. Ignacio Ribas y Marques and Joaquin de Pascual Terera, "Reaction of Organic Sulfides with Aqueous Gold Chloride Solution", Ion. 4, 31, 73-8 (1944).
10. Davidson, N. and Brown, H., "The Polymerization of Some Derivatives of Trimethyl Aluminum", J. Am. Chem. Soc. 64, 316-24 (1942)
11. Prafulla, C. R. and Nadiabehari, A., "Complex Compounds of Iridium", J. Ind. Chem. Soc. 9, 251-7 (1932).
12. Hodgman, C. D. "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., 29th edition, (1945).
13. Ljunggren, Gustaf and Norberg, B., The Effect and Toxicity of Dimethyl Sulfide", Acta Physiol. Scand. 5 248-55, (1943) Chem. Zentr. 1943, II, 1979.
14. Reilly, J. and Ray, W. N. "Physico-Chemical Methods", Methuen and Co., Ltd., London, 2nd edition, 1933, Ch. 59.
15. Fonteyne, R. "Infra Red and Raman Spectra of Polyatomic Molecules", J. Chem. Phys. 8, 56-9, (1940).
16. Glasstone, S., Theoretical Chemistry", D. Van Nostrand Co., N. Y., (1944). p. 410-22.
17. Osborn, D. W., Doescher, R. N. and Yost, D. M., "The Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, and Entropy of Dimethyl Sulfide", J. Am. Chem. Soc. 64, 169-73 (1942)
18. Osborn, D. W. Doescher, R. N. and Yost, D. M., "The Entropy of Dimethyl Sulfide from Low Temperature Calorimetric Measurements. Restricted Rotation of the Methyl Groups", J. Chem. Phys. 8, 506 (1940).
19. Hunter, E. and Partington, J. R., "Studies in Dielectric Polarization", J. Chem. Soc. 2820, (1932).
20. Sugden, T. M., Walsh, A. D., and Price, W. C., "Ionization Potentials of Poly Atomic Molecules", Nature, 148, 372-3 (1941).

THE INTERHALOGENS AND RELATED COMPOUNDS

Elliot N. Marvell November 19, 1946

Introduction:

The halogens form an extensive series of compounds among themselves and ako with the so-called halo genoids or pseudo-halogens. Most of these compounds are not well known and have not been intensively investigated. This is due perhaps to the instability and extreme reactivity of many of them. The literature has been rather thoroughly surveyed and a general compilation of their preparations are reactions is presented here.

A. The Interhalogens:

I. Type AB (References 1-25)

All the possible combinations of the halogens as halogen monohalides have been shown to have a definite existence except iodine monofluoride.

Preparations:

For the preparation of ICl, IBr, and BrCl equimolar portions of the requisite halogens are mixed and allowed to stand for varying periods of time. The reaction between iodine and chlorine goes to completion, but the latter two reactions produce only equilibrium mixtures. IBr has never been isolated whereas BrCl has been obtained in an impure condition by fractional distillation at low temperatures. The reactions between chlorine or bromine and fluorine form in each case more than one compound and the desired products have been obtained pure through distillation and fractional condensation.

Reactions:

With olefines: - both ICl and BrCl add to the double bonds in olefines with great ease.

substitutions in organic molecules: - ICl is a well known iodinating agent for sensitive organic compounds, while IBr acts as a brominating agent on the same type of compounds.

with water: - ICl may be hydrolyzed in two ways with the formation of HOI, or HIO_3 and iodine in the two cases. BrCl forms a stable hydrate containing four molecules of water. The fluorides of chlorine and bromine react explosively with water.

as oxidizing agents: - ICl reacts as a weak oxidizing agent with positive iodine atom being reduced to iodine or to iodide ion depending on the strength of the reducing agent.

as acids: - IBr has been investigated as an acid in iodine solution. Thus, neutralization can occur with the acid IBr and the base KI with the formation of solvent iodine and salt KBr.

II. Type AB_3 (References 26-32)

Preparations:

The only known compounds in this group are ICl_3, IBr_3, BrF_3 and ClF_3. If the required halogens are mixed in the

proper amounts, all the above compounds can be isolated either directly or by distillation except IBr_3 which has not yet been prepared in the pure state.

Reactions:

As oxidizing agents: - ICl_3, ClF_3 and BrF_3 are all oxidizing agents. The trivalent halogen atom may be reduced either to free halogen or to halide ion. The oxidizing power increases in order $I < Br < Cl$ which is in reverse order to their stability in the trivalent state.

with water: - BrF_3 reacts with water to produce oxygen while ClF_3 attacks water explosively.

decomposition: - BrF_3 is quite stable while the other three compounds of this type decompose to form the lower compound and free halogen. This is especially noticiable with IBr_3.

addition reactions: - alkalie fluorides and organic amine hydrofluorides add ICl_3 to form stable addition complexes.

III. Type AB_5 (References 33-38)

Preparations:

Fluorine, which is noted for its ability to force elements into their higher valence states, combines with bromine and iodine in the pentavalent condition. The reaction with bromine must be run at high temperatures whereas iodine reacts in the cold.

Reactions:

with alkalie: - alkalie reacts with the pentafluorides forming alkalie fluorides and bromate or iodate as the case may be.

with organic compounds: - IF_5 acts as both an iodinating and a fluorinating agent on organic molecules.

with halogen: -

$$BrF_5 + Cl_2 \xrightarrow{300^\circ} BrF_3 + 2ClF$$

V Type IF_7 (39,35)

Preparation:

IF_7 is the only compound of this group.

$$IF_5 + F_2 \xrightarrow{270-300^\circ} IF_7 \qquad 83\% \text{ yield}$$

Reactions:

with alkalie: - When IF_7 reacts with alkalie the products may be either iodate and oxygen or periodate depending on the conditions.

with halogen: - The reaction by which IF_7 is produced is reversed in the presence of I_2.

The Pseudohalogen halides:

I. The cyanogen halides: (References 56-68)

Preparations:

Halogens react with alkalie cyanides to produce all the cyanogen halides except FCN. FCN can be formed under anhydrous conditions from ICN and AgF.

Reactions;

polymerization: - all the cyanogen halides except FCN trimerize to form cyanuric trihalides.

with base: - the cyanogen halides react with bases with the production of alkalie cyanates and halides.

with ammonia: - cyanogen halides and ammonia form ammonium halides and cyanamide.

II. The halogen ozides (40,41,55,69)

Preparations:

Halogens react with silver and alkalie azides to form halogen azides. The reaction requires anhydrous conditions.

Reactions:

With hydroxyl ion: - The reactions of halogen azides with hydroxyl ions produce hypohalous acid and azide ion.

as oxidizing agents: - If the halogen atom of the halogen azides is considered as a positive halogen it can act as an oxidizing agent, being reduced in the process to halide ion.

III. Oxy, Thio and Selcnocyanogen halides (References 42-47; 50-53)

Preparations:

oxycyanogen halides can be prepared by the action of halogens on silver cyanate. Thiocyanogen halides may be produced from thiocyanogen or from lead thiocyanate.

Reactions:

polymerization: - all the oxycyanogen halides form dimers of the form

$$X_2N - \overset{O}{\overset{\|}{C}} - N = C = O$$

oxidation: - these compounds may be considered as possessing positive halogen atoms which can act as oxidizing agents.

C. The Interpseudohalogens (48, 49, 54)

Preparations:

$BrCN + NaN_3 \longrightarrow NaBr + N_3CN$

$ICN + AgCNS \longrightarrow AgI + CN - SCN$

$Br_2C(CN)_2 + 2NaN_3 + H^+ \xrightarrow{\text{ether}} C_2N_8$

Reactions;

Dimerization: -

$2\ CN_4N_3 \longrightarrow N{\equiv}C - N{=}C(N_3)_2$ The general reactions of cyanazide are those of the dimer.

References

. Cerdeiras, Anales soc. espan fis.quim. 13, 460 (1915)
. Tarugi, Gazz. chim. ital. 48I, 1 (1918)
. Fournean & Donard, Compt. rend. soc. biol. 81, 1192 (1918)
. Delepine & Ville, Bull Soc. Chem. 27, 673 (1920; Compt.rend.170, 1390 (1920)
. Fourneau & Donard, Bull. Sci. Pharmacol. 27, 561 (1920)
. Lang, Z. anorg. allgem. chem. 122, 332 (1922)
. Bodenstein & Schmidt, Z. Physik. Chem. 123, 28 (1926)
. Fillipov, Z. Physik 6, 1024 (1928)
. Ruff, etal., Z. anorg. allgem. chem. 176, 258 (1928)
. Barratt & Stein, Proc. Roy. Soc. 122A, 582 (1929)

11. Ruff, etal., Z angew. Chem. 41, 1289 (1929)
12. Gillam & Morton, Proc. Roy. Doc. 124A, 604 (1929)
13. Loomis & Allen, Phys. Rev. 33, 639 (1929)
14. Lux, Ber. 63B, 1156 (1930)
15. Taylor & Forscey, J. Chem. Soc. 1930, 2722
16. Jost, Z. physik. Chem. 14B, 413 (1931)
17. Cornog & Karges, J. Am. Chem. Soc. 54, 1882 (1932)
18. Anwar-Ullah, J. Chem. Soc. 1932, 1176
19. Ruff, etal., Z. anorg. allgem. Chem. 207, 46, (1932)
20. Ruff & Braida, ibid 214, 81 (1933); ibid. 214, 91 (1933)
21. Vesper & Rollefson, J.Am. Chem. Soc. 56, 620 (1934)
22. Miltzer, J. Am. Chem. Soc. 60, 256 (1938)
23. Fialkov & Goldman, J. Gen. Chem. USSR 11, 910 (1941)
24. Cornog & Bauer, J.Am. Chem. Soc. 64, 2620 (1942)
25. Cornog & Olson, ibid. 62, 3328 (1940)
26. Lebeau, Ann.Chem. Phys. [8], 9, 241 (1906)
27. Hanzlik & Tarr., J. Pharmacol 14, 221 (1919)
28. Birk, Z. angew. Chem. 41, 751 (1928)
29. Ruff & Krug., Z anorg. allgen. Chem. 190, 270 (1930)
30. Truesdale & Beyer, J. Am. Chem. Soc. 53, 164 (1931)
31. Ruff, etal, Z. anorg. allgem. Chem. 206, 59 (1932)
32. Forbes & Faull, J. Am. Chem. Soc. 55, 1820 (1933)
33. Sidgewick, J. Chem. Soc. 125, 2672 (1924)
34. Ruff & Menzel, Z. anorg. allgem. Chem. 202, 49 (1931)
35. Ruff & Braida, Z. angew chem. 47, 480 (1934)
36. Ruff & Braida, Z. anorg. allgem. Chem. 220, 43 (1934)
37. Simons, Bond & McArthur, J. Am. Chem. Soc. 62, 3477 (1940)
38. Ruff & Keim, Z. anorg. allgem. Chem. 201, 245 (1931)
39. Ruff & Keim, ibid 193, 176 (1930)
40. Audubert & Ralea, Compt. rend. 208, 983 (1939)
41. Hantzsch, Ber. 33, 524 (1900)
42. Cornog, etal, J. Am. Chem. Soc. 60, 429 (1938)
43. Kaufmann, Oel, Kohle, Erdoel & Teer 14, 199 (1938)
44. Baroni, Atti acad Lincei 23, 871 (1936)
45. Kaufmann, Ber. 60B, 58 (1927)
46. Lecher & Joseph, Ber. 59B, 2603 (1926)
47. Kaufmann, Ber. 57B, 973 (1924)
48. Ott & Weisenburger, Ber. 70B, 1829 (1937)
49. Hart, J. Am. Chem. Soc. 50, 1922 (1928)
50. Birckenback & Linhard, Ber, 64B, 961 (1931)
51. Birckenback & Linhard, Ber. 63B, 2528 (1930)
52. Birckenback & Linhard, Ber. 63B, 2544 (1930)
53. Birckenback & Linhard, Ber. 62B, 2261 (1929)
54. Walden and Audrieth, Chem. Rev. 5, 339 (1928)
55. Spencer., J. Chem. Soc. 127, 216 (1925)
56. Perret & Perrot, Bull. Soc. Chim. 7, 743 (1940)
57. Slotta, Ber. 67B, 1028 (1934)
58. Oberhauser & Schormuller, Ber. 62B, 1436 (1929)
59. Oberhauser, Ber. 60B, 1434 (1927)
60. Klemenc & Wagner, Z. anorg. allgen. Chem. 235, 427 (1938)
61. Zappi, Bull Soc. Chim 47, 453 (1930)
62. Sernagiotto, Giom. Chim. ind. applicata 3, 153 (1921)
63. Manguin & Simon, Compt. rend. 169, 474 (1919)
64. Cormasti, Anales asoc quim. argentina 27, 45 (1939)
65. Zappi & Labriola, Bull Soc. Chim. 5[5], 27(1938)
66. Zappi, Anales asoc. quim. argentina 21, 37 (1933)
67. Mooney & Reid, J. Chem. Soc. 1933, 1318
68. Gosslett, Z. anorg. allgem. Chem. 201, 75 (1931)
69. Oberberger, Inorganic Seminar, November 6, 1945
70. Hofer & Wiig, J. Am. Chem. Soc. 67, 1441 (1945)

SUPERCONDUCTIVITY

Carlyle E. Shoemaker - November 26, 1946

I. Discovery

As each new low temperature was reached, one of the easiest and first measurements to be made was the resistance of various metals. Kammerlingh-Onnes discovered superconductivity or the phenomena of no resistance by measuring the resistance of mercury at the temperature of liquid helium. The temperature at which the metal loses its resistance is defined as the transition temperature.

II. Super conducting Elements

A. Location in Periodic Table

				Al	
				1.14°	
	Ti	V --------	Zn	Ga	
	1.81°	4.3	0.79°	1.07°	
	Zr	Cb---------	Cd	In	Sn (white)
	0.7°	9.22°	0.54°	3.37°	3.69
La	Hf	Ta---------	Hg	Tl	Pb
4.71°	0.35°	4.38°	4.12°	2.38°	7.26
	Th				
	1.3-1.4°				

B. Conclusions

1. All superconducting elements have 2-5 electrons in the outer shell.
2. No superconductors have been found among monovalent metals, transition metals of Group VIII ~~(except La)~~ or the rare earth metals~~(except La)~~
3. Atomic volumes of superconducting elements lie in a close range.
4. Nearly all types of crystal symmetry are found.

III. Alloys and Compounds

In addition to the above elements, various alloys and compounds of other elements are superconducting. A few examples are:

Alloys: Au_2Bi 1.8°
Carbides: MoC 7.7°, Mo_2C 2.4°, WC 2.8, W_2C 2.05°
Sulfides: CuS 1.5°
Nitrides: Bi_3N 3.6°

Alloys and compounds of superconducting elements are also known. In general an alloy containing a superconducting element has a lower transition temperature than the superconducting component. Eutectic alloys of Tl, Pb, Sn with elements in VB have transition temperatures higher than those of the constituents. X ray examination of Sn-Tl alloys indicates that the lattice dimensions are a maximum at the eutectic composition and the transition temperature is at a minimum.

IV. Factors affecting the transition temperature.

A. A large current will cause a superconductor to resume its normal properties. This is thought to be due to the magnetic field which accompanies the current.

B. A magnetic field restores a superconductor to its original state. The field necessary increases with de-

creasing temperature (below transition temperature) Meissner and Ochsenfeld found that a residual magnetic field could be "frozen" in a hollow superconductor. They also concluded that no residual magnetic field could exist in a pure superconductor though this is not true for an alloy or an impure element.

C. The shape and stresses cause slight changes in the transition temperature.

V. Possible changes in structure accompaning the transition.

A. X ray diffraction patterns of lead are unable to detect any changes in the structure.

B. Discontinuous changes are observed in the specific heats of tin and thallium.

C. Thermodynomically, a latent heat should be observed but this point is controversial.

D. Thermal conductivity shows a change which is not general.

E. There is no theromolectric effect between two metals when both are superconductors. Effects decrease until they are zero at the transition temperature (within experimental measurements). There is a thermoelectric effect between a superconductor and a nonsuperconductor of the same metal when one is kept in the normal state by a magnetic field.

F. No changes observed in the photoelectric effect, in the absorbtion of β particles or slow electrons, no appreciable change in the reflectivity for visible light, or in the absorption of long infra red radiation; experiments are limited however.

G. Several instances of a time lag at the transition temperature have been reported. This may indicate that the superconducting phase is different from the normal phase and that growth started from nuclei at the transition temperature.

VI. Conclusions

It is thought that changes at the transition temperature affect only the conduction electrons, for the properties which are significantly different in the superconducting and the normal states all depend on these electrons.

Bibliography

1. Burton, E. F., Smith, H. Grayson, Wilhelm, J. O. "Phenomena at the Temperature of Liquid Helium" Reinhold Pub. Corp. (1940)
2. Koch, K. H., Kolloid Z. 105, 89-97 (1943).
3. Koch, K. H., Z. Physik. 120, 86-102 (1942).
4. Andronikashvili, E. L., Compt. rend. acad. sci. U.R.S.S. 31, 541-2 (1941).
5. Alekseevskii, N., J. Phys. (U.S.S.R.) 9, 217-21 (1945).
6. Sharvin, J. Phys (USSR) 9, 350-1 (1945).
7. Lazarev, B., Galkin, A., J. Exptl. Theoret. Phys. 14 474-80 (1944).
8. Lazarev, B., Kan, L., J. Phys. (U.S.S.R.) 8, 361-70 (1944).
9. London, F., Nature 137, 991 (1936).

THE SILICON OXYHALIDES

Roy E. Dial November 26, 1946

Introduction

Friedel and Ladenberg (1), in 1868, first prepared Si_2OCl_6 (hexachlorodisiloxane) by passing $SiCl_4$ over white hot feldspar, $KAlSi_3O_8$, in a porcelain tube. Troost and Hautefeuille (2) prepared a series of oxychlorides in 1876 by passing a mixture of chlorine and oxygen over heated silicon. The results are questionable except for Si_2OCl_6 and $Si_4O_4Cl_8$ which were confirmed by Rheinboldt and Wisfield (3) in 1935. The investigation of the oxyhalides apparently lay dormant from 1868 until Rheinboldt and Wisfield revived it.

Oxyiodides

No evidence of formation of oxyiodides was found.

Oxybromides

Rheinboldt and Wisfield (3) determined the optimum reaction temperature for the reaction of oxygen on $SiBr_4$ (to form oxybromides) to be between 670-695°C. Higher temperatures than 695° result in the formation of SiO_2. Si_2OBr_6 and $Si_4O_4Br_8$ were prepared.

Schumb and Klein (5) prepared a series of oxybromides as follows:

A. Dry air was bubbled through a trap of bromine and this mixture passed over silicon (97.5% pure) which was contained in a tube in a furnace at 700°.

B. Oxygen was passed over $SiBr_4$ at 670 - 695°.

		% Products in A	% Products in B	M.P.	B.P	Other Properties
1	Si_2OBr_6	20.6	14.4	27.9°	118° (15m.m.)	Colorless liquid " crystals
2	$Si_3O_2Br_8$	49.4	29.6	17.5°	159° (13m.m.)	Colorless liquid " crystals.
3	$Si_4O_4Br_8$	1.0	30.4	123°	155° (7m.m.)	Colorless liquid white solid
4	$Si_4O_3Br_{10}$	12.4	10.4	-91°	122° (<.5m.m.)	Colorless liquid glassy solid
5	$Si_5O_4Br_{12}$	10.3	9.6	-82°	150° (<.5m.m.)	Colorless liquid glassy solid
6	Residue	6.2	5.3	-78°	160-180° (<.5m.m.)	Colorless heavy oil glassy solid

Oxychlorides

Schumb and Holloway (4) prepared a series of oxychlorides by passing a mixture of two volumes of chlorine and one volume of oxygen over silicon (98% pure) heated to a red heat in a pyrex tube, slanted so that the tube could be moved as the reaction proceeded along the tube. The mixtures were fractionated in a Podbielniak type distillation column.

The compounds obtained all had the following properties: increased viscosity with increased complexity; miscible with CCl_4, CS_2, $CHCl_3$ or $SiCl_4$; incombustible; they hydrolyze in moist air, the lower ones more readily.

	M.P.	B.P.	Other Props.
$SiCl_4$	-70	57	Colorless liquid
Si_2OCl_6	-28.1	137	Colorless, oily liquid
$Si_3O_2Cl_8$	-70	76(15m.m.)	Colorless, oily liquid
$Si_4O_4Cl_8$	77	91(15m.m.)	Colorless, cryst solid
$Si_4O_3Cl_{10}$		109-110 (")	Colorless, oily liquid
$Si_5O_4Cl_{12}$		130-131 (")	Colorless, oily liquid
$Si_6O_5Cl_{14}$		138-141 (")	Colorless, oily liquid
$Si_7O_6Cl_{16}$		145-147 (")	Colorless, oily liquid

Schumb (6) shows that $SiCl_4$ (diluted with anhydrous ether) can be hydrolyzed by a moist organic solvent (like ether) to form appreciable amounts of oxychlorides.

Latimer and Hildebrand (3) give the following reactions:

$$2SiCl_4 + 2SO_3 = Si_2OCl_6 + S_2O_5Cl_2$$

$$SiCl_4 + 3SO_3 = SiO_2 + 2S_2O_5Cl_2$$

Oxyfluorides

Booth and Osten (7) fluorinated Si_2OCl_6 with an excess of SbF_3, using up to 15% SbF_5 as catalyst, at room temperature and low pressure. Oxyfluorides and a large amount of SiF_4 were obtained. The mixture was sublimed from one ampule to another, then distilled in a low temperature distilling column to remove all of the silicon fluoride. The rest of the liquid was distilled at atmospheric pressure to separate it into fractions and to obtain a distillation curve, which was automatically recorded by a Micromax recording potentiometer. Each fraction was then distilled several times at pressures between 100 mm. and 1 atm.

	$Si_2OF_3Cl_3$	$Si_2OF_4Cl_2$	Si_2OF_6
B.P., °C	42.9	16.8	-23.3
M.P., °C	-100.0±.05	-60.0±.05	-47.8±.05
Liq. range, °C	143	76.8	25.3
Liq. density	1.467	1.432	1.358
Mol. wt., obsd.	236	232	184.5
Mol. wt., calcd.	235	219	186.0
$\Delta H_{vap.}$, cal., calcd.	7300	6770	5150
Trouton const.	23.1	23.3	20.6

Si_2OClF_5 and $Si_3O_2F_8$ were also believed to have been obtained. The presence of SiF_4 is believed to be due to the hydrolysis of Si_2OCl_6.

The general properties of these compounds are as follows: they hydrolyze in water or alkaline solutions; their odors are similar to that of SiF_4; they do not attack mercury, copper or nichrome at ordinary temperatures; they are clear liquids white solids; and the liquidus ranges for the chlorofluorides are greater than for the fluorides.

Since $F_3SiOSiF_3$ is an anolog of ethers, it might be expected to have the properties of an ether and to coordinate with BF_3, but the analogy is only formal.

Zachariassen (11) determined the structure of titanite, $CaTiSiO_5$. The 22 oxygen atoms of the unit cells are in three different kinds of positions (O_I, O_{II}, and O_{III}), where O_I is not connected to any SiO_4 group. Zachariassen and Strunz predicted that water (OH) and fluorine play a noticeable role in the lattice, and that they are substituted for O_I.

Sahama (12) determined the fluorine content of titanites from six different localities. The fluorine is probably bound as CaF_2, because no fluorine is given off when the sample is heated with CaF_2 and quartz. He investigated titanite under the microscope, and could find no fluorite, CaF_2, even though the sample was rich in fluorine. Therefore, he explained the fluorine as being in the titanite structure itself.

Machin and Vanecek (13) showed that additions of small amounts (1-4%) of fluorspar is very effective in reducing fiber diameters of mineral wool produced from melts of MgO, CaO, Al_2O_3 and SiO_2. Mechanism of the action of fluorspar in lowering the viscosity of molten slags is explained on the network theory of Zachariassen.

Miscellaneous

Isolation of higher members is difficult due to the small quantities obtained, the difference between the boiling points of adjacent members and the percentage difference in composition becoming smaller, and viscosity and decomposition on distillation becoming greater.

Compounds of the form $SiOX_2$ have not been isolated and probably do not exist, because the Si=O link polymerizes spontaneously to form the Si-O-Si linkage.

The Si-O-Si bond is the only stable type of bond formed by the loss of water from the polyhydroxy compounds.

In general, the insertion of an oxygen atom between two silicon atoms modifies the volatility to only a slight extent.

Pauling says that the Si-Cl bond is partially double bond in character (about 50%), and that the Si-F bond is partially triple bond in character.

References

1. Friedel and Ladenberg, Compt. Rend. 66, 539 (1868).
2. Troost and Hautefeuille, Ann. Chim. Phys. 5, 7, 452 (1876).
3. Rheinboldt and Wisfield, Ann. 517, 197 (1935).
4. Schumb and Holloway, J. Am. Chem. Soc. 63, 2758 (1941).
5. Schumb and Klein, J. Am. Chem. Soc. 59, 261 (1937).
6. Schumb, Chem. Rev. 31, 587 (1942).
7. Booth and Osten, J. Am. Chem. Soc. 67, 1092 (1945).
8. Latimer and Hildebrand, "Reference Book of Inorganic Chemistry Chap. XIV Macmillan and Co., New York (1940).
9. Pauling, "Nature of the Chemical Bond", pp. 53, 228-235 Cornell Univ. Press, Ithaca (1945).
10. Ph.D. Thesis, James Hartt, Western Reserve University, (1945)
11. Zachariassen, Zeit. Krist., Abt.A, Bd. 73, 7 (1930).
12. Sahama, "Bulletin de la Commission geologique de Finlande" No. 138, pp. 88-120, (1940).
13. Machin and Vanecek, Illinois State Geol. Survey, Rept. Investigations No. 68, 15 pp. (1940).
14. Grigorev and Iskyul, Bull. acad. sci U.R.S.S. Classe. sci. math. nat., Ser. geol. 1937, 77-106 C.A. 33, 3726 (1939).
15. Grigorev, Mem. soc. russe mineral 66, 118-23 (1937) C.A. 33, 3726 (1939).

PREPARATION OF SOLID ELEMENTS IN A STATE OF PURITY

December 3, 1946

Karl M. Beck

Introduction

During the last fifteen or twenty years considerable progress has been made in methods of obtaining solid elements in a high state of purity. Most of these processes have been designed for use on a laboratory scale so that purity of product was the prime consideration rather than expense and yield. These developments have made possible many refinements, corrections, and additions to studies of the properties of the elements. The high degree of purity has been described by such terms as "super-purity metals", and is usually well over 99%. The determination of purity is by difference. The impurities are determined spectroscopically and subtracted, so the impurities present must be known.

The most concise manner of summarizing this work is by considerating methods which have been used with appropriate examples. More detailed data are readily available in a book by van Arkel (1) in which each element is considered.

Thermal decomposition of compounds

This has not been one of the most applicable methods in the past, but it is becoming more important because of its simplicity and small requirements on apparatus.

1. Na, K, Rb, and Cs (4) have been prepared by decomposition of their azides in high vacuum at 275-395°. The metals can be further purified by distillation in the same apparatus, and are obtained spectroscopically pure and gas-free.

2. Pt, Pd, and Ir of about 99.995% purity can be obtained by decomposition of their ammonium chloro-metallate salts, $(NH_4)_2MCl_6$; Rh from $(NH_4)_3Rh(NO_2)_6$, Ru from $RuNOCl_3.NH_4Cl$, Os from H_2OSCl_6 (5).

3. Ductile Ta can be prepared by heating rods of TaO_2 to a high temperature with electric current (6).

4. Spectroscopically pure Ge can be prepared by decomposition of Ge_3N_4 at 1000°. The nitride is obtained from $GeCl_4$ plus NH_3 to get the imide, which with nitrogen at 350° forms the nitride (7).

5. Pure graphite crystals 10 x 30 x 30 Å, can be prepared by heating sucrose in a stream of hydrogen at 1000-1100° for 10 hours.

Work is now being done on the decomposition of organometallic compounds as a possible source of many metals.

Hot-wire methods

Perhaps the most outstanding modern development in this field of pure elements is the invention of the hot-wire technique. It was used successfully in 1925 by van Arkel and de Boer, and has been expanded rapidly since by these two men and several other investigators.

In this method a volatile compound is decomposed or reduced at the surface of a wire which is heated by an electric current. The wire is preferably made of the element being de-

posited, but may be of another suitable material. The apparatus usually consists of a glass or quartz bulb with sealed in leads connected to the wire, a connection to the vacuum system and a supply of the compound to be decomposed, and a trap for volatile products (8).

1. Cu, Ti, Zr, Hf, Th, V, Cr, Mo, W, Re, Fe, and Ni can be prepared by decomposition of their halides at 600-2000°. These metals lend themselves particularily well to "continuous reaction", in which the liberated halogen reacts with a supply of the metal, in powdered form prepared fairly pure by another method.

2. Be, Si, V, and B have been prepared by reduction of volatile halides by hydrogen.

3. Ta, Cb, and Pt can be prepared by decomposition of halides, or carbonyl halide in the case of Pt.

This method has its greatest value in preparing high melting elements which are difficult to obtain pure by other methods, such as Ti (ductile), Zr, Hf, Th, Cb, Ta, Re, and B. There are experimental difficulties such as maintaining a constant temperature in the wire which is constantly increasing in diameter; the current may have to be increased from an initial fraction of an ampere to a final several hundred amperes. Apparatus is not simple, yields are often low, and only small quantities of the element can be prepared in a run, so this method in many cases is used as a last resort.

Reduction methods

Reduction of oxides and halides to obtain pure elements is one of the oldest methods, but there have been some interesting progress in techniques and some novel reducing agents.

1. Fe, Co, and Ni can be prepared by reduction of their oxides with hydrogen. Ferric oxide is reduced this way commercially to produce Fe which is 99.994% pure (9). MoO_2 is reduced by hydrogen at 900-1200° to pure Mo. Ammonium per-rhenate is readily reduced to metallic Re, and 99.85% pure V can be made by reduction of VCl_3 with hydrogen.

2. Chromic oxide can be reduced to Cr in two ways (10). With hydrided tantalum at 1000° a good product results. Or 99.95% pure Cr can be obtained by heating the oxide with CaH_2 at 470°. In the latter case the Ca liberated reacts with the water produced, so the reduction is complete inabout 30 minutes.

3. Th, Be, V, and B can be prepared by reducing their oxides with calcium hydride.

4. Cr, Th, U, and V can be prepared by reduction of their oxides or chlorides with metallic calcium. Pure ductile Ti and Zr can be prepared by reduction of their dioxides with Ca in a fused bath of $CaCl_2$-$BaCl_2$. Rb and Cs halides can be reduced with Ca by using special techniques, but the reaction is not very useful.

5. Zr has a high affinity for oxygen and the oxide formed is very refractory, so Zr is a good, although expensive, reducing agent. Rb, K, Cs, and Li can be obtained by reduction of their chromates or sulfates with zirconium (25), and the products

are very pure. The reductions go at moderate temperatures giving no volatile products.

Electrolytic methods

Many metallic elements can be conveniently prepared by electrolysis of their salts in aqueous or fused salt solutions.

1. Ga is best prepared by electrolysis of $Ga(OH)_3$ in NaOH solution using Pt electrodes (11). The temperature is kept above 30° so the liquid Ga formed can be collected in a cup below the cathode.

2. Pure Th can be prepared by electrolysis of an aqueous solution of thorium sulphamate.

3. U, Th, Ta, and Cb can all be prepared by electrolysis of melts containing complex fluorides of the metals. U obtained from KUF_5 is deposited on a Mo cathode, and is 99.88% pure. In obtaining Ta and Cb from K_2MF_7 some pentoxide of the metal being deposited is added to overcome the anode effect.

4. Ce, La, Nd, Pr, Sm, and Gd have been prepared by electrolysis of their fused chlorides (13) in purities of 94-98%, except Gd which is obtained 99% pure. This coupled with reduction of oxides by alkali or alkaline earth metals and with amalgam formation has permitted isolation of most of the rare earth elements in a fairly pure state.

5. Sc has been prepared by electrolysis of a fused KCl-LiCl-$ScCl_3$ mixture using a tungsten cathode (14).

Separation of similar elements by chemical means

Certain closely similar elements can best be separated by chemical methods to obtain one or more of them in a pure state.

1. Sc can best be separated from the rare earths and thorium by extraction of an acid solution of the mixture containing H_4SCN with ether. A large quantity of 75-80% Sc_2O_3 ore after such treatment had 90% of the Sc extracted in spectroscopically pure form.

2. Eu, Sm, and Yt can be separated from the other rare earths by shaking a solution of the acetates with sodium amalgam (15), the Eu, Sm, and Yt being concentrated in the amalgam layer. Yt has been removed from Nd-Sm and Sm-Gd mixtures this way, and Yt and Eu can successfully be removed from a Sm-Eu-Gd mixture by sodium amalgam. There is also an electrolytic method of amalgam formation (16, 26).

3. Investigations of separating rare earths by means of base-exchange methods with zeolites, by liquid-liquid extraction of covalent compounds such as the thiocyanates, and by chromatographic separation processes are being investigated, and the zeolite method appears especially promising.

4. Zr and Hf are still best separated by fractionation. After purification by recrystallization of phosphates, ferrocyanides, or oxysulfates followed by a couple of recrystallizations of the oxychloride, Zr salts which are spectroscopically free of Hf have been obtained.

Purification methods

Many metals can be prepared in "commercially pure" states and then further purified on a laboratory scale by one of several methods.

1. By distillation--Many solid elements can be purified by distillation in high vacuum. Cr, Al, Si, Be, Fe, Cu, Ni, Sn, and Pb have been purified thus (19), the Be being only 99.89% pure, but the others in higher purity. Be which is 99.95% pure can be obtained by special distillation methods at 1900° from a sintered BeO crucible. Zn which has less than 0.0001% total impurities is obtained by distillation purification (20). Te containing Se, Cu, Fe, and some oxide is purified by distillation in vacuum.

2. By sintering or fusion in vacuum--Sintering and vacuum fusion are especially useful for removing volatile impurities from metals of high melting point. Ductile Ta and Cb can be prepared this way (21), either by pressing the powdered metal into bars and sintering in vacuo just below the melting point, or by making the hydride and decomposing it at 1500°. Cathodic Ni is purified by annealing in H_2 at 1050° to remove C and S, and then fusing in vacuum in magnesia crucibles to get 99.94% pure Ni.

3. By electrolytic methods-- Cu which is 99.999% pure is made from commerically pure copper by electrolysis in a H_2SO_4-$CuSO_4$ bath, air-blowing to remove S, and finally electrolysis using $Cu(NO_3)_2$ as an electrolyte. Indium which is 99.999% pure is prepared from commerically pure indium by electrolysis using $InCl_3$ as an electrolyte. Zn, Pb, Mn, and Ag are prepared especially well by electrolysis.

4. Special methods--- Certain difficult elements require special methods of purification. Iodine is purified of other halogens and organic matter by sublimation in a current of oxygen over Pt at 700° (22). The Fe and silica are removed from Si by special acid treatment. American sulfur is freed of organic matter by a method using MgO and redistillation.

Preparation of elements in special allotropic forms

It is interesting to note that of the twelve diamonds prepared by Hannay (23) in 1879-1880 from paraffin, bone-oil, and lithium, eleven have been shown by X-ray analysis to be true diamonds.

Recently black phosphorus was prepared from the white allotrope by application of pressure of 100,000 kg./sq. cm. at room temperature.

References

1. A. E. van Arkel, Reine Metalle Herausgegeben, Springer, Berlin (1939)
2. Wright, et al, Proc. Amer. Soc. Test. Mat., 37 I, 531, 538 (1937)
3. Welch, Ann, Reports on Progress of Chem., 40, 68 (1943)
4. Suhrmann and Clusius, Z. anorg. Chem., 152, 52, (1936)
5. Wichers, Gilchrist, and Swanger, Trans. Amer. Inst. Min. Met. Eng., 76, 602 (1928)
6. C. W. von Bolton, Z. Electrochem., 11, 45 (1905)
7. Schwarz, Die Chemie, 55, 45 (1942)
8. Laubengayer, et al, J. Am. Chem. Soc., 65, 1924 (1943)
9. Adcock, J. Soc. Chem. Ind. (Transactions), 59, 28, (1940)
0. Alexander, Met. and Alloys, 5, 37 (1934)
1. Sebba and Pugh, J. Chem. Soc., 1937, 1371
2. Lloyd and Pugh, ibid, 1943, 8
3. Trombe, Ann. Chim., 6, 349 (1936)
4. Fischer, et al, Z. anorg. Chem., 231, 54 (1937)
5. Marsh, J. Chem. Soc., 1942, 398, 523
6. McCoy and Hammond, J. Am. Chem. Soc., 64, 1009 (1942)
7. Willard and Freund, Ind. Eng. Chem. (Anal.), 18, 195 (1946)
8. Russell and Pearce, J. Am. Chem. Soc., 65, 1924 (1943)
9. Kroll, Metal Ind. (London), 47, 3, 29, 103, 155 (1935)
0. Truesdale and Edmunds, Amer. Inst. Min. Met. Eng., Inst. Metals Divn., 133, 267 (1939)
1. Smithells, Metal Ind. (London), 38, 336 (1931)
2. Baxter and Lundstedt, J. Am. Chem. Soc., 62, 1829 (1940)
3. Hannay, Proc. Roy. Soc. (London), A30, 188, 450 (1880) A32, 407 (1882)
4. Gunther, et al, Z. anorg. Chem., 250, 373, (1943)
5. de Boer, Broos, Emmers, ibid, 191, 113 (1930)
6. Inorganic Syntheses, I, page 15, McGraw-Hill, New York, (1939) Jukkola, Audrieth and Hopkins

STRUCTURES OF THE PHOSPHATES

O. F. Hill December 3, 1946

Introduction. The chemistry of the phosphoric acids and their salts is very complex and, even now, not very well understood. The evident confusion in the literature has reached a stage where a thorough understanding of the structure of the phosphates is most desirable and where a logical approach and a new working hypothesis are necessary. It has only been during the last two decades that such phosphate structure studies have been undertaken and only in the last few years that any extensive studies have been reported. Though advances in a practical and a theoretical way have been made, there is still much work to be done to bring order into this chaotic field.

Phosphates can be grouped into three major classes: orthophosphates, polyphosphates, and metaphosphates. These have been listed in Table 1. Phosphates of composition varying all the way from phosphorous (V) oxide to the orthophosphates have been reported, though many of these are subject to question. Indeed some of higher phosphorous content than required for the met phosphates have been reported, as for example, $CaO \cdot 2P_2O_5$ and $2CaO \cdot 3P_2O_5$ the existence of which has been established beyond doubt (1).

TABLE 1

The Phosphates

Class of Phosphates	Formula of the acid	Remarks
Orthophosphates	H_3PO_4	Most stable of all phosphates. Structure fairly well established. May be prepared by dissolving P_2O_5 in water.
Pyrophosphates	$H_4P_2O_7$	Undergo slow hydrolysis to orthophosphates. Structure well established. The sodium salt may be prepared by igniting Na_2HPO_4.
Tripolyphosphates (Triphosphates)	$H_5P_3O_{10}$	Undergo slow hydrolysis to orthophosphates. Structure fairly well established. The sodium salt may be prepared by fusing mixtures of a) NaH_2PO_4 and Na_2HPO_4 or b) $(NaPO_3)x$ and $Na_4P_2O_7$.
Tetraphosphates	$H_6P_4O_{13}$	Existence questionable
Metaphosphates	$(HPO_3)_x$	Undergo hydrolysis to orthophosphates with pyrophosphates as intermediate products. Structure quite complex and not well understood. See Table 2 for added information.

Structures.

Phosphorous (V) Oxide, P_4O_{10}. P_4O_{10} is the product obtained upon complete oxidation of phosphorous. Inconsistent data were obtained in the early studies of the vapor pressure of P_4O_{10} (2). Subsequent studies (3,4,5,6) led to the conclusion that at least two crystalline modifications exist, as well as a glass. Later experimenters (7) showed that actually there are three distinct crystalline modifications which differ, not only in their physical properties, but also in their chemical properties. These three forms are the hexagonal, m.p. 422±6°C.; orthorhombic, m.p. 558±6°C.; and tetragonal(?), m.p. 580±5°C.

The hexagonal form is metastable with respect to both the orthorhombic and the tetragonal (?) forms and is the form widely known to chemists. It reacts vigorously with water. The orthorhombic form is metastable with respect to the tetragonal (?) form and is surprisingly resistant to water, a suspension dissolving only slowly, even at steam-bath temperatures. The tetragonal (?) form is the stable form and reacts with water quickly with the liberation of much heat to be converted into a stiff gel which shortly liquefies to a limpid liquid. This difference in reactivity is undoubtedly due to differences in structure.

The crystals of the hexagonal form (8) consist of agglomerates of P_4O_{10} molecules whose structure is the same as that of the P_4O_{10} vapor phase as determined by Hampson and Stosick (9) from electron diffraction data. The four phosphorous atoms are bound together through oxygen atom linkages to form a regular tetrahedron. Each phosphorous atom is then tetrahedrally surrounded by four oxygen atoms.

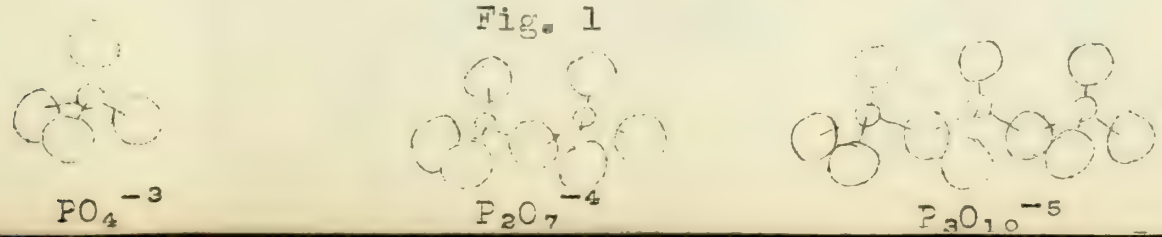
The orthohombic form is an infinite sheet polymer containing interlocking rings (10). Crystal structure determinations have not been made on the tetragonal (?) form, though indications are that it is an infinite polymer of either a three dimensional type or a sheet type. The tetragonal symmetry makes the sheet type improbable.

Orthophosphates. It is pretty well established that the orthophosphate structure consists of a phosphorous atom tetrahedrally surrounded by four oxygen atoms. (11,12,13). The crystal structures are such that the coordination number of the cations, as well as that of the phosphorous, is satisfied by bonds to oxygen. For example, the crystal structure of KH_2PO_4(14,15) may be regarded as consisting of HO_2,PO_4, and KO_8 groups interconnected so as to satisfy the valency relations.

Pyrophosphates. The pyrophosphate structure may be regarded as consisting of two PO_4 tetrahedra sharing an oxygen atom at one corner as in the Si_2O_7 group (11,12,16). The structure of ZrP_2O_7 consists of four molecules per unit cell (11,18)

Tripolyphosphates. The tripolyphosphate structure may be considered as an extension of the pyrophosphate structure, three PO_4 tetrahedra joined through corners into a chain (13).

Fig. 1



Metaphosphates. Less is known about the structures of the metaphpsphates than any of the others. It is highly probable that there is no monomeric form. However, polymers ranging from dimers to hexamers and even higher have been reported (13,19,20). Many of these seem fairly certain and others are somewhat doubtful. The trimer is established with certainty. A dimer, tetramer, and hexamer probably exide. A higher polymer is obtained by heating NaH_2PO_4 below fusion for a long period of time. Methods of preparation and properties of the different metaphosphates are listed in Table 2.

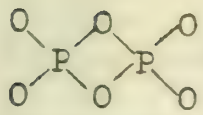
TABLE 2(20)

The Sodium Metaphosphates

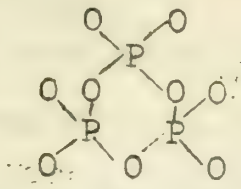
Name	Probable Polymer	Methods of Preparation	Properties
Pascal's Salt	?	$(C_2H_5PO_3)_x + C_2H_5ONa$ in ether soln	White deliquescent solid; sol. in water; ppts. with Ag^+, Pb^{++}, Ca^{++}; coagulates albumin.
Sodium dimetaphosphate	di	1. Heat H_3PO_4 a short time at ca. 300°, neutralize cold soln 2. Heat NH_4NO_3(1 pt.), NaH_2PO_4(5 pts.), and NH_4Cl(1 pt.) at 250°	Sol. in water but hydrolyzes rapidly to pyrophosphate; ppts. with Pb^{++} but does not coagulate albumin.
Maddrell's Salt	?	Heat NaH_2PO_4 at 300-400° for several hrs.	Crystalline, insol. solid; two crystalline modifications.
Knorre's Salt or Sodium trimetaphosphate	tri	1. Heat NH_4NO_3(1 pt.) and NaH_2PO_4 (2 pts.) at 300°. 2. Heat NaH_2PO_4 at 500 600° for several hrs. 3. Heat fused Graham's salt at 300-400° for several hrs.	White, sol. cryst. subst., m.p. 625°; no ppt. with Ag^+ or Pb^{++} in low concn; no ppt. with Ca^{++}, coagulates albumin.
Sodium tetrametaphosphate	tetra	Heat CuO and H_3PO_4 up to 400°. Treat Cu salt with H_2S and neutralize.	White sol. subst; ppts. Pb^{++} and Ca^{++} but not Ag^+ coagulates albumin.
Graham's Salt or Sodium hexametaphosphate	hexa?	NaH_2PO_4, $Na_2H_2P_2O_7$, or $NaNH_4HPO_4$ fused and quenched	Easily sol. glass; ppts with Ag^+ and Pb^{++}, but forms stable complex ion with Ca^{++}
Kurrol's Salt	>hexa	Obtained sometimes on heating NaH_2PO_4 below fusion for long periods of time. Potassium salt made readily by heating to above 300°.	Insol. in water but dissolves in solns of pyro-and hexametaphosphates to give highly viscous solns. Melts at 809° to give liq. distinct from Graham's salt. The cooled melt is an insol. glass.

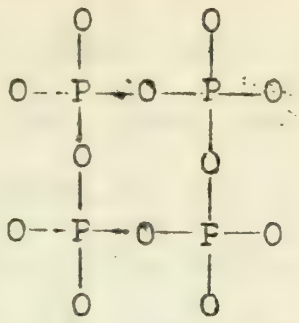
The most likely structural configurations for th metaphosphates (21,22) are given by the structu l formulae in Fig. 2. These structures are those which best fit the known chemical properties.

Fig. 2

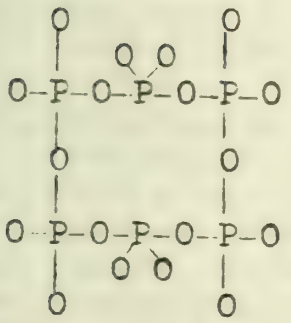


dimetaphosphates
(21)

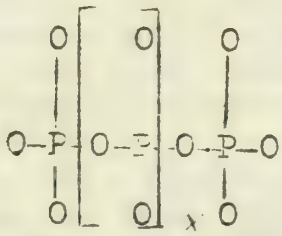




tetrametaphosphate
(25)



hexametaphosphate
(22)



Higher polymers
of metaphosphates
(23)

Molecular weight determinations on the glassy polymers have indicated values from 10,000 to 20,000, the exact molecular weight being a function of the length of time of heating and the temperature of heating (13,23,24)

$Al(PO_3)_3$ is the only metaphosphate the crystal structure of which has been determined (26). The unit cell consists of 16 $Al(PO_3)_3$ molecules. It has a tetrametaphosphate structure, that is, there are four PO_4 tetrahedra in a ring. AlO_6 octahedra share the remaining oxygen atoms of the PO_4 tetrahedra.

Theoretical. With the knowledge of the structure of P_4O_{10} and of the phosphates we are now able to examine the reactions which occur when the bonds in these structures are broken. A theoretical treatment should prove to be very illuminating and helpful in the interpretation of available data.

For example, if a statistical analysis is made of the bond ruptures which may occur when water reacts with P_4O_{10}, one may make some predictions as to the composition of the resulting acid. It is possible to calculate theoretically concentrations of orthophosphoric, pyrophosphoric, tripolyphosphoric, and metaphosphoric acids which might be expected for products of varying $P_4O_{10}:H_2O$ ratios. This has been done and the data compared with analytical results obtained by Bell (27) of the Victor Chemical Works. The agreement insofar as the more complex acids is concerned is not good, but it is certainly in the right order of magnitude for the orthophosphoric acid, which might be expected to be present in such equilibrium mixtures. The disagreement which is noted between calculated and observed components of such $P_4O_{10}:H_2O$ mixtures may not be real in that it is not known how the compositions subjected to analysis were obtained. Whether true equilibrium is attained in any $P_4O_{10}:H_2O$ composition between various components has not been established. Furthermore, a statistical treatment, such as outlined above, assumes equal bond energies

BIBLIOGRAPHY

1. Hill, W. L., Faust, G. T., and Reynolds, D. S., Am. J. Sci, 242, 457, 542 (1944).
2. Smits, A. and Rutgers, A. J., J. Chem. Soc. 125, 2573 (1924)
3. Smits, A. and Dernum, N. W., Z physik. chem. (A)149, 337 (1930)
4. Smits, A., Ketelaar, J.A.A., and Meyering, J. L., Z. physik. Chem. (B)41, 87 (1938).
5. Hoeflake, J.M.A. and Scheffer, F.E.C., Rec. trav. chim. 45 191 (1926).
6. Southard, J.C. and Nelson, R. A., J. Am. Chem. Soc. 59, 911 (1937).
7. Hill, W. L., Faust, G. T., and Hendricks, S. B., J. Am. Chem. Soc. 65, 794 (1943).
8. deDecker, H.C.J. and MacGillavry, C.H., Rec. trav. chim. 60, 153 (1941).
9. Hampson, G. C. and Stosick, A. J., J. Am. Chem. Soc. 60, 1814 (1938).
10. deDecker, H.C.J., Rec. trav. chim. 60, 413 (1941).
11. Pauling, L., The Nature of the Chemical Bond, Cornell University Press, Ithaca, New York, 1945, p. 249.
12. Wells, A.F., Structural Inorganic Chemistry, Oxford Press, London, 1945, p. 417.
13. Quinby, O.T., Chem. Rev. (submitted for publication).
14. Hendricks, S.B., Am. J. Sci; 241, 269 (1927).
15. West, J., Z. Krist. 74, 306 (1930).
16. Schweitzer, G. K., Inorganic Seminar, October 15, 1946.
17. Levi, G. R. and Peyronel, G., Z. Krist. 92, 190 (1935).
18. Peyronel, G., Z. Krist. 94, 311 (1936).
19. Karbe, K. and Jander, G., Koll. Beihefte 54, 1 (1942).
20. Yost, D.M. and Russell, N., Jr., Systematic Inorganic Chemistry Prentice-Hall, Inc., New York, 1944, p.211.
21. Treadwell, W.D. and Leutwyler, F., Helv. Chim. Acta 21, 1450 (1938).
22. Rudy, H. and Schloesser, H., Ber. 73, 484 (1940).
23. Samuelson, O., Svensk Kem. Tid. 56, 343(1944); C.A. 40, 4613 4 (1946).
24. Malgren, H. and Lamm, O., Z. anorg. Chem. 252, 256 (1944).
25. Nylen, P., Z. anorg. allgem. chem. 229, 30 (1936).
26. Pauling, L. and Sherman, J., Z. Krist. 96, 48 (1937).
27. Bell, Victor Chemical Works (unpublished data).

COMPLEX FORMATION WITH HIGH MOLECULAR WEIGHT AMINES

Higgins, Norton A. December 10, 1946

I. Introduction

There are many literature references on the general subject of complex compounds involving amines and metal salts; however until this year no reports have listed compounds of high molecular weight aliphatic amines (1). Only within the past few years have these amines been available, and a study was instigated by the Research Laboratory of Armour and Company because of the great difference in properties between the low and high molecular weight amines.

II. Preparation

The methods of preparation necessarily differ from those in use for the preparation of complex compounds containing low molecular weight amines. Most metal salts are insoluble in organic solvents, while on the contrary, the high molecular weight amines are in all cases insoluble in water. Furthermore, the amines are unable to displace water from metal-salt hydrates, and the salts employed must therefore be carefully dried before use. The preparation is usually carried out by mixing an alcoholic solution of the metal salt with an alcoholic solution of the amine. The complex precipitates and is recrystallized. When this method fails, other procedures such as heating the reactants in absence of solvent may be used.

III. Properties

Several high molecular weight amine complexes have been prepared. Variations of the metal have included: copper, silver, zinc, cadmium, and mercury. Variations of the amine have included: dodecylamine, octadecylamine, and dioctylamine. The complexes are low-melting (75°-155°) solids, insoluble in cold water. They are decomposed by hot water to yield free amine, metal oxide or hydroxide, and probably amine hydrochloride and basic metal salt. Thus about one-half of the amine may be recovered by steam distillation from a mixture of water and bis-(dodecylammino) cupric chloride.

IV. Amine-metal Ratio

Every complex prepared has been found to have an amine-metal ratio of 2:1. It is possible with copper salts to obtain substances of a deeper blue color than the 2:1 complexes, but these cannot be obtained in the crystalline state. The explanation for the failure of the amines to fill the coordination sphere probably lies in their great bulk.

In addition to the complex compounds, two double salts were prepared during the course of this study; cupric dodecylammonium chloride and cupric octadecylammonium chloride. They resulted when an excess of cupric chloride was added to the amine. In this case the blue complex was not formed; rather there precipitated a yellow product with a Cu:Amine:Cl ratio of 1:2:4, which proved to be $CuCl_2 \cdot 2AHCl$ (A represents amine). The salts differed strikingly from the complexes since they melted

above 200° and were soluble in water. The amine:cu ratio in the salts, as in the complexes, is 2:1, but for a different reason. The yellow-brown color of anhydrous $CuCl_2$, its concentrated alcoholic solution, and its hydrochloric acid solution have been ascribed (2) to the presence of the $(CuCl_4)^{=}$ ion. By analogy the yellow alkylammonium double salts may be considered to contain this grouping. Thus the 2:1 ratio is necessitated by the 4-coordination power of copper: $(CuCl_4)(AH)_2$.

V. Dissociation of Complexes

Broome, Ralston, and Thornton (3) desired to apply the Method of Continuous Variations as expanded by Vosburgh and Cooper (4) to the amine complexes to determine whether any ratios other than 2:1 were to be found. In the course of this investigation it was found that the complex dissociated to an extent of about 10 per cent at room temperature in 0.04 molar chloroform solution. This dissociation prevented the use of the Method of Continuous Variations. Thus while ratios higher than 2:1 may exist, the question is still an open one.

References

1. Broome, Ralston, Thornton, J. Am. Chem. Soc., 68, 67 (1946).
2. Moeller, J. Phys. Chem., 48, 111 (1944).
3. Broome, Ralston, Thornton, J. Am. Chem. Soc., 68, 849 (1946).
4. Vosburgh, Cooper, J. Am. Chem. Soc., 63, 437 (1941).

STABILITY OF CHELATE COMPOUNDS

I. Introduction

Although a great deal of work has been done in the preparation of chelate compounds and upon their structure, no attempt has been made until recently to determine quantitatively how structural factors of the organic residue other than simple geometry influence the stability of chelates. Calvin, along with Wilson, Bailes, and Duffield, in a recent series of three papers (1) (2) (3) has brought to light several factors which play an important role in the stability of chelate complexes.

II. Factors Influencing Stability

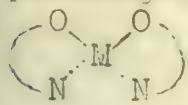
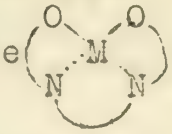
A. Acid Strength of Chelate Group

Experiments involving the equilibrium $Cu^{++} + 2Ke^{-} \rightleftharpoons CuKe_2$ have indicated that the acid strength of the chelating organic residue influences the stability of the complex in an inverse sense. Thus complexes of weakly acidic organic groups are more stable than those of strongly acidic organic groups.

B. Possibility of Enolate Resonance

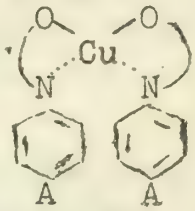
The chelate ring involving the central metal atom is thought to exist as a resonance hybrid. If another resonating structure, such as the benzene ring, be fused to the chelate ring, the chelate resonance is to a greater or lesser extent hindered (as in salicylaldehyde, for example). Any interference with the resonance of the chelate decreases proportionately the stability of the complex.

C. Joining Together of Chelate Groups

The joining together of chelate groups exerts a pronounced stabilizing effect on the complex. Studies involving polarographic reduction have shown that compounds of the type  are more readily reduced than those of the type  .

The half-wave potential for the first type is about +0.02v., while that of the second type is -0.75v.

D. Availability of the Coordinating Electron Pair

An investigation of compounds of the type  has shown that as constituent A is changed in the order NO_2, SO_3Na, phenyl, H, CH_3, OH, and OCH_3 there is an uniform increase in the stability. This is just the order of increasing base strength of the corresponding aniline and the order of availability of the electron pair on the coordinating nitrogen.

References

1. Calvin, Wilson, J. Am. Chem. Soc., 67, 2003 (1945).
2. Calvin, Bailes, ibid, 68, 949 (1946).
3. Duffield, Calvin, ibid, 68, 557 (1946).

ALKALINE EARTH AND HEAVY METAL SOAPS

T. H. Vial

December 17, 1946

Metallic soaps are salts of complex monobasic organic acids. The soaps of the alkali metals, except lithium, are water soluble, while those of the alkaline earths and heavy metals are water insoluble, but usually soluble in non-polar solvents.

The organic raw material may be animal or vegetable fats or oils, or the free fatty acids derived therefrom, napthenic acids, or rosins. Napthenic acids are found in certain petroleum crudes. They are carboxylic acids of varying molecular weight, usually containing a five-membered ring in the carbon chain. Rosin gives rise to rosin acids and rosin oils, both of which find use in soaps for special uses.

The inorganic raw materials are salts of the desired metal. There is much less variation in properties in these than in the organic material. The commonly used salts include oxides, hydroxides, carbonates, acetates, chlorides, sulfates, and nitrates.

Metallic soaps may be of either the precipitated or the fused type. In the former, a solution of the sodium soap is allowed to react with a solution of appropriate metallic salt. If (FA) represents the fatty acid radical, the reaction may be represented as follows:

$$2Na(FA) + CoSO_4 \longrightarrow Co(FA)_2 + Na_2SO_4$$

The sodium soap shown above may arise directly from the hydrolysis of fat or oil, or by the neutralization of the free fatty acid.

Fused soaps are prepared by the same type of reaction chemically, but the physical technique is quite different. Either an oil or a fatty acid is allowed to react with an oxide, a hydroxide, an acetate, or a carbonate by heating the two to a relatively high temperature in the absence of added water. With free fatty acids the reaction may be represented:

$$M(OH)_2 + 2H(FA) \longrightarrow M(FA)_2 + 2HOH$$

The salt is so chosen that the second product of the reaction (water in this case) will be volatile at the temperature of the reaction.

For convenience, the uses to which soaps are put may be divided into three classes --uses depending on the available metal present, uses based on their ability to influence the characteristics of liquids, and uses based on physical characteristics of the soaps. The largest quantities of soaps are used for purposes which depend on the available metal present. The acid anion serves to make the metal most readily available under the conditions of its use. Catalysis requires a high degree of subdivision so as to obtain a large surface area. Soaps offer solubility in organic solvents, giving almost molecular subdivision. Most of the use of soaps as catalysts to date has been in the paint and the petroleum industries. In the paint industry metallic soaps are used to catalyze the oxidation (and polymerization) of drying oils. In the petroleum industry soaps are used as addition agents to lubricating oils. They were once considered anti-oxidants, but there are indications that they

catalyze the total oxidation of the lubricant to volatile products, leaving the lubricant sludge-free. Some, napthenates for example, have been shown to act as anti-oxidants at atmospheric temperatures and as prooxidants at engine temperatures.

Other uses based on the metal present include fungicides, ceramic glazes, and analytical agents.

Uses based on ability to influence characteristics of liquids include applications as wetting and dispersing agents, detergents (in nonaqueous solvents, e.g. in the dry cleaning industry), emulsifiers, and in greases. The uses based on the physical properties of the soap include flatting and anti-chalking agents for paints, means of applying monomolecular films, special lubricants, and cosmetics.

References

S. B. Ellicott, The Alkaline-Earth and Heavy-Metal Soaps, Reinhold Publishing Corp., New York, N. Y., 1946

A. S. G. Lawrence, Trans. Faraday Soc., 34, 660 (1938)

V. L. Shapp, Oil Gas J., 34, (44) 56 (1936); J. Inst. Petroleum Tech. 22, 567A (1936). (Napthenic acids)

F. A. Gerardi, J. Chem. Education 10, 415 (1933) (Rosin acids)

CONTACT CATALYSIS

January 7, 1947 Agnes McDonald

Prior to 1920 many technological processes were based upon the ability of prepared solid surfaces to induce chemical reactions between gases. Theoretical knowledge of the processes, however, was limited almost entirely to the observations made by Faraday in 1834 (1). Langmuir's concepts of contact catalysis had been published, but they attracted very little attention at first. These concepts proved to be the stimulus for the investigations which brought contact catalysis out of the realms of mystery.

The development of the theories of contact catalysis can be divided into four phases of study (1).

A. Langmuir's concepts of unimolecular adsorption and the kinetic treatment of catalytic reactions:

Langmuir states (2,3,4) that all forces involved in the structure of solids and liquids are chemical in nature. Not only chemical combinations, but the phenomena of condensation, adsorption, condensation, etc. are manifestations of primary and secondary valences. The valency of the atom is divided among the surrounding atoms. Thus, there is an unbalanced force on the surface of a catalyst and the atoms are loosely bound. Since chemical forces are of short range, the unsaturated crystals on the surface will adsorb a monolayer of gas. The amount of gas adsorbed depends on a kinetic equilibrium between condensation and evaporation. Probably every molecule hitting the surface condenses and evaporates. Adsorption might be considered the lag between condensation and evaporation. At first, these ideas were considered as speculation, but experimental investigations proved them to be essentially correct (5-11).

B. Heterogeneity of the catalyst surface and the concept of activity centers:

Langmuir's concepts could not be applied unaltered to heterogeneous surfaces (12-16). There is a wide range of efficiency in reactions. In some reactions every atom will be active, in other reactions relatively few are active. It is evident that adsorption is dependent upon factors other than available surface atoms. Taylor suggested (5) that only a small portion of the catalytic surface is necessarily active. Catalysis may be confined to certain active centers. Interaction apparently takes place when molecules of two gases are adsorbed on adjacent atoms of the catalyst.

C. Inner nature of adsorption:

The concept of activity centers could not be fully developed until a distinction was made between chemical and physical adsorption. This distinction was necessary to help explain why some good adsorbents are poor catalysts and some poor adsorbents are good catalysts. Benton and White (28) observed that at certain pressures the adsorption of hydrogen on nickel increased with increasing temperature. These observations were plausible if the lower temperature adsorption were physical and the higher temperature adsorption were chemical. The isotherms indicated that three reactions were involved (a) chemical adsorption, (b) physical adsorption, (c) solution of gas and metal. The chemisorption of gases requires an activation energy which is furnished by the rising temperatures. Quantum mechanical calculations (32) indicate that this energy of activation is a function of the group spacing .

D. Extent of surface area of the catalysts and the significence of the several kinds of crystals on catalytic activity:

A comprehensive study of contact catalysis has been presented by Brunauer and Emmett (38, 41). Their studies are limited to the synthesis of ammonia but "their methods have become a norm for expressing numerically the accessible surface of a solid body" (1). Other methods have been used to verify this method.

The geometric arrangement of a surface has a definite relation to the activity of the surface. A surface activited for one reaction may not be activated for another: Beeck and coworkers (39,44) have shown that there is a definite relation between the efficiency of the catalysts and optimum spacing of the atoms.

Tracer elements, magnetic characteristics of the catalysts and the gases adsorbed, and the rate of adsorption at various pressures are used to study the process of making and breaking bonds at a prepared surface.

References

1. Taylor, Am. Sci., 34, 554-72 (1946)
2. Langmuir, Phys. Rev., 6, 79-8 (1915)
3. Langmuir, J. Am. Chem. Soc., 38, 221-95 (1916)
4. Langmuir, Proc. Nat. Acad. Sci., 3, 251-7 (1917)
5. Taylor, Proc. Roy. Soc. (London), 113A, 77-86 (1922)
6. Boswell and McLaughlin; Tran. Roy Soc. (Canada), 17, SectIII. 1-20 (1923)
7. Pease, J. Am. Chem. Soc., 45, 2296-2305 (1923)
8. Beebe and Taylor, J. Am. Chem. Soc. 46, 435 (1924)
9. Pease and Yung, J. Am. Chem. Soc. 46, 390-403 (1924)
10. Taylor, J. Phys. Chem. 28, 898-942 (1924)
11. Henshelwood and Prichard; J. Chem. Soc. 127, 17-36, 1546-52, 1552-9, 2896-2900 (1925)
12. Almquist, Gaddy, Bronam, Ind. Eng. Chem., 17, 599-603 (1925)
13. Pease and Stewart, J. Am. Chem. Soc., 47, 1235-40 (1925)
14. Taylor and Russell, J. Phys. Chem. 29, 1325-41 (1925)
15. Almquist, J. Chem. Education, 3, 385-9 (1926)
16. Almquist and Black, J. Am. Chem. Soc., 48 2814-6 (1926)
17. Tweedy, Chem. and Ind., 45 157-9; 177-80 (1926)
18. Tweedy, Proc. Roy. Soc. (London), 112A 296-303 (1926)
19. Beebe, J. Phy. Chem., 30, 1538-44 (1926)
20. Pease and Griffin, J. Am. Chem. Soc. 49 25-81 (1927)
21. Pease and Stewart J. Am. Chem. Soc. 49 2783-7 (1927)
22. Rideal, Chem. Reviews 5 67-84 (1928)
23. Taylor. Ind. Eng. Chem. 20 439-443 (1928)
24. Langmuir, Chem. Reviews 6 451-79 (1929)
25. Taylor and Lavin, J. Am. Chem. Soc. 52 1910-18 (1930)
26. Taylor, J. Am. Chem. Soc., 52 5298-9 (1930); 53 578-97 (1931)
27. Taylor and McKinney, J. Am. Chem. Soc. 53 3604-24 (1931)
28. Benton and White:, J. Am. Chem. Soc. 52 2523-36 (1930) 53, 2807-8, 3301-14 (1931); 54 1373-90 (1932)
29. Taylor. Trans. Faraday Soc. 28 131-8 (1932)
30. Rideal, Trans. Faraday Soc. 28 139-47 (1932)
31. Taylor and Long, Phys. Rev. 40 463-4 (1932)
32. Taylor, Eyring and Sherman, J. Chem. Physics 68-76 (1933)
33. Russell and Ghering, J. Am. Chem. Soc. 57 2544-52 (1935)
34. Palmer and Clark, Proc. Roy Soc. (London) A149 360-84 (1935)
35. Rideal, Proc. Roy. Soc London. A-155 684-90 (1936)
36. Rideal and Eley, Proc. Roy. Soc. (London) A178 429-5 (1941)
37. Taylor, Trans. Electrochem. Soc. 71, 375-381 (1937)
38. Emmett and Brunauer., Tran. Electrochem Soc. 71 383-394 (1937)
39. Beeck, J. Chem. Phys. 4 680-9 (1936) 5 268-73 (1937)
40. Taylor., J. Chim. phys. 34 529-35 (1937)
41. Brunauer and Emmett, J. Am. Chem. Soc. 59 2682-9 (1937)
42. Taylor, Nature 144 8-9 (1939)
43. Twigg and Rideal, Trans. Faraday Soc. 36 533-7 (1940)
44. Beeck, Wheeler, Smith. Phys. Rev. 55 601-2 (1940)

THE ROLE OF THE CATALYST IN THE SANDMEYER REACTION

John Speziale

January 14, 1947

The Sandmeyer reaction is the replacement of a diazonium group by a halogen atom using cuprous halide and a halogen acid.

Side reactions usually give rise to phenols, biaryls and azo compounds. Hodgson (1) has postulated separate mechanisms for halogen substitution and the side reactions, whereas Waters (2) has postulated a single mechanism.

Cuprous halides react with diazonium salts mainly by:

1. The formation of a complex anion with halogen acid; attraction of the complex anion to the diazonium cation; release of an electron from the halogen to the nitrogen via the significant carbon atom followed by separation of neutral chlorine and evolution of N_2; linkage of neutral chlorine to the aryl radical followed by rehabilitation of the complex anion by corrdination with an external chloride ion.

2. Oxidation of Cu^{+} to Cu^{++} by diazonium ion, which involves release of an electron by the copper to the nitrogen with subsequent linkage of the aryl radicals produced to form biaryls.

A. $Cu^{+} + Ar - \overset{+}{N}\equiv N: \longrightarrow Cu^{++} + Ar. + N_2$

B. $2Ar. \longrightarrow Ar- Ar$

But if the reaction is carried out in an acid medium then Waters submits the following for halogen substitution:

C. $Ar. + Cl^{-} \longrightarrow ArCl + e$

D. $Cu^{++} + e \longrightarrow Cu^{+}$

Waters and Hodgson are in agreement only on equations A and B. This mechanism differs from that of Hodgson for the Sandmeyer reaction in that Hodgson postulates that electron transfer takes place in reverse of phase C and that there is an electron release at the significant carbon atom of the aryl group from a chlorine atom of the complex anion $(CuCl_4)^{=}$.

Mechanism 1 as postulated by Hodgson also serves to explain the results in a mixed Sandmeyer reaction. Eight aryl amines were diazotized and then decomposed in two ways.

(a) CuCl dissolved in concentrated HBr
(b) CuBr dissolved in concentrated HCl

Table I
Mixed Sandmeyer Reaction

Amine	(a) CuCl in HBr		(b) CuBr in HCl	
	%Bromo	%Chloro	%Bromo	%Chloro
-nitroaniline	90	10	31	69
-nitroaniline	96	4	32	68
-nitroaniline	96	4	36	64
-phenylenediamine	96	4	31	69
enzidine	93	7	35	65
-chloroaniline	94	6	35	65
-bromoaniline	92	8	37	63

The difference in the percentage of bromo to chloro compounds in (a) and (b) can be explained on the basis of the complex anions $(CuClBr_3)^{\equiv}$ and $(CuCl_3Br)^{\equiv}$. The mechanism is similar to that for $(CuCl_4)^{\equiv}$. In similar experiments, using CuI in HCl and HBr it was shown that the iodo compound was formed predominantly. Thus in these mixed copper complexes, the order of reactivity is I > Br > Cl.

In order to test the contention of Hantzsch and Blagden (3) that the halogen comes from the inorganic salt and not from the diazonium halide, Hodgson (1) treated a diazonium salt with cuprous halide in aqueous suspension and in methyl sulfide solution in the absence of acid. The results showed that when (a) CuCl reacted with p-bromobenzene-diazonium bromide, the main product was p-chlorobromo-benzene and (b) when CuBr reacted with p-bromobenzenediazonium chloride, the main product was p-dibromobenzene. According to his mechanism, a complex anion is formed between the cuprous halide and the coordinating solvent in water or methyl sulfide. The halogen from the diazonium salt will replace the departing halogen from the anionoid complex, and give rise to a small amount of the other halogen derivative.

In aqueous solution, hydrofluoric acid is assumed to be largely H_2F_2 (ionized as $H^+ + HF^-_2$) and a small amount of HF (not ionized). These properties account for the ineffectiveness of copper as a catalyst since the affinity of fluorine for hydrogen and stability of the HF^-_2 anion apparently prevent complex cuprous formation. The small yield of fluoro compound (25% from diazotized m-nitroaniline) would, therefore, appear to be due to attack of cationoid carbon by nonionized HF, the HF^-_2 ion being unreactive like chloride and bromide ions.

When, however, a dry borofluoride is decomposed by heating ArN_2BF_4 the same kind of process occurs as in the cuprous salt mechanism - a polarized fluorine atom in BF_4^- ion attacks the cationoid carbon like Cl in the $(CuCl_4)^{\equiv}$ complex with the resulting evolution of N_2 and BF_3 and subsequent replacement of the diazonium group by fluorine.

Hodgson (4,5) found that cupric salts were as effective as cuprous salts in the Sandmeyer reaction. The Sandmeyer reaction appears to be dependent upon the degree of positivity of the diazonium ion, which when of sufficient magnitude enables the more ephemeral cupric halogen comolexes to react like their cuprous analogues. The complex cupric anion is postulated as hydrated $(CuX_4)^{=}.2H_2O$ which serves to activate the otherwise stable halide ions.

The reaction of cupric chloride is general for properly substituted aryl diazonium chlorides. When the significant carbon atom has only a relatively small postive charge (as in diazotized aniline and toluidines) cupric chloride is practically ineffective. But for those amines which have a nitro or halogen group in the ring, the significant carbon atom will bear a relatively high positive charge due to the (+I) inductive effect. In these cases cupric chloride is as effective as cuprous chloride.

Most of the decompositions of diazonium halides hitherto studied have been in acid solution and found to vary greatly in concentration of acid. It appeared of interest to ascertain whether chloride ions take part in the decomposition (6).

The acid solution of p-nitrobenzenediazonium chloride was exactly neutralized with the appropriate base and the corresponding metallic chlorides added in equivalent amount to secure parallel sets of decompositions.

Table II

Effect of chloride ion on p-$NO_2C_6H_4N_2Cl$

Base	Salt	%Yield - p + $NO_2C_6H_4Cl$
nil	nil	28
$CaCO_3$	nil	6
ZnO	nil	5
$CaCO_3$	$CaCl_2$	12
ZnO	$ZnCl_2.2H_2O$	6
$NaHCO_3$	NaCl	3
K_2CO_3	KCl	6
$CaCO_3$	$CuCl_2.2H_2O$	85

In the foregoing table, the addition of metallic chlorides causes no significant rise in yield of the chloro compound. The only exception is when hydrated cupric chloride is added to the neutral solution of the diazonium salt. According to Hodgson this indicates the presence of the complex cupric anion $(CuCl_4)^=$ held to exist in acid solution. These results are claimed to show that the chloride ion plays little, if any, part in the substitution of chlorine for the diazo group, since the only cases of appreciable substitution are those in which there is the possibility of the existence of covalent chlorine (or partly polarized) with HCl, $CaCl_2$ and $CuCl_2$.

Reactions were carried by decomposing diazotized m- and o-nitroaniline in concentrated HCl using metallic chlorides whose metals are prone to form complex halogen anions (7).

All decomposition were carried out under identical conditions.

Table III

Effect of metallic chlorides on p-$NO_2C_6H_4N_2Cl$

Addition	%Yield p-$NO_2C_6H_4Cl$
HCl	54.4
$AlCl_3$	60.7
$SbCl_3$	37.1
$CaCl_2$	54.4
$CrCl_3$	54.4
$CoCl_2$ blue sol.	70.9
$CoCl_2$ pink sol.	10.2
Blank without $CoCl_2$	10.2
$CuCl_2$	77.6
$CuCl_2$	77.6
$FeCl_3$	77.6
$HgCl_2$	54.4
$NiCl_2$	60.7
$SnCl_4$	60.7
$ZnCl_2$	54.4

It is seen that both cupric chloride and ferric chloride are as efficient as cuprous chloride.

The experiments with cobaltous chloride have an interesting bearing on its ionic state - when anhydrous or in a solution of

high chloride ion concentration, cobalt chloride is blue owing to the presence of $(CoCl_4)^=$ anion and such a solution affords a 70.9% yield of the chloro compound. The more aqueous pink solution containing $(Co(H_2O)_6)Cl_2$ gives about 10% yeild, the same dilution but with no cobaltous chloride present. These experiments with $CoCl_2$ support the interpretation that the decomposition is due to $(CuX_4)^-$.

Sandmeyer was unable to isolate any intermediate complex. Hodgson suggests that the complex salt $(ArN_2)_2\ CoCl_4$ existed in his experiments with cobaltous chloride. The efficiency of ferric chloride in concentrated HCl was due to the formation of the complex ferric salts ArN_2FeCl_4. Several double salts of diazonium chlorides have been reported (8).

Hodgson and Sibbald (9) have reported eight examples of these complex ferric salts. They decompose when heated with concentrated HCl, giving the aryl chloro compound. This is further evidence for the Hodgson mechanism. These complexes are yellow-orange crystalline solids, soluble in water. Cold solutions are stable but decompose upon heating. The dry solids can be kept from a few days to one year without decomposition.

Hodgson summarizes his work on the Sandmeyer reaction as follows:

1. Cuprous salts do not possess unique characteristics as claimed by Sandmeyer and Waters.
2. In cases where the diazonium cation possesses sufficient positivity, cupric salts can function with efficiency comparable to those of cuprous salts.
3. Metals other than copper can form anionoid complexes with halogen which decompose in like manner to the copper salts.
4. There are no fundamental differences in the mechanism of formation of halogen compounds during the decomposition of complex diazonium chlorides with cuprous chloride, cupric chloride, zinc chloride or any other chloride (including HCl) in aqueous or other media. Such differences as do occur are due to differences in stability and concentration of the complex anion whereby the competing action of anionoid water can become negligible (cuprous salts) or predominant (zinc salts).
5. All the reactions can be interpreted by the single anionoid mechanism already proposed.

BIBLIOGRAPHY

1. Hodgson, Birtwell & Walker, J. Chem. Soc., 1941 770.
2. Waters, J. Chem. Soc., 1942, 266.
3. Hantzsch & Blagden, Ber., 33, 2544 (1900).
4. Hodgson, Birtwell & Walker, J. Chem. Soc., 1942, 720.
5. Hodgson, J. Chem. Soc., 1946, 745.
6. Hodgson & Sibbald, J. Chem. Soc., 1945, 545.
7. Hodgson, Birtwell & Walker, J. Chem. Soc., 1944, 18.
8. Schmidt & Maier, J. prakt. Chem. 132 153 (1931).
   Saunders, The Aromatic Diazo Compounds. Longman & Green, London 1936, pp. 37, 154.
9. Hodgson & Sibbald, J. Chem. Soc., 1945, 819.

Roy D. Johnson

February 11, 1947

I. Introduction (1)

Although early workers believed that organo metallic compounds could not be formed by the metals in groups six and seven of the periodic chart, a very interesting series of organo-chromium compounds has been prepared and studied by Hein and his coworkers. The basic reaction for the preparation of the entire series of compounds has been the reaction of chromic chloride or chromyl chloride with a cold aryl Grignard solution. The resulting aryl compounds closely resemble the inorganic dichromates in color, are relatively unstable thermally, and are quite sensitive to oxygen and light. No instance of alkyl-Chromium compounds being isolated was found.

II. Phenyl-Chromium Compounds

Hein's original work (2) in the field was in the synthesis and study of phenyl-Cr compounds. Ph_5CrBr (2,3) is the chief product when $CrCl_3$ or CrO_2Cl_2 and PhMgBr react in ice cold ether (some Ph_4CrBr and Ph_3CrBr are also formed).

$$CrCl_3 + 5PhMgBr \xrightarrow{Et_2O} Ph_5CrBr + 3CrCl_2 + 3MgCl_2 + 2MgBr_2$$

$$CrO_2Cl_2 + 5PhMgBr \xrightarrow{Et_2O} Ph_5CrBr + 2Mg_2OBr_2 + MgCl_2$$

Formation of Cr^{II} compounds has been confirmed (4) by the formation of hydrogen on acidification. Since hydrogen is liberated also in water or sodium acetate solutions, Hein has suggested the formation of univalent Cr in the following manner:

$$4CrCl_2 + 4PhMgBr \longrightarrow Ph_4CrCl + 3CrCl + 2MgCl_2 + 2MgBr_2$$

$$\text{then } CrCl + H_2O \longrightarrow Cr(OH)_2Cl + H_2$$

The crude product was purified by the formation and subsequent decomposition of an $HgCl_2$ addition product. It is a typical organo-Cr compound, as it is orange in color and gives an immediate precipitate of AgBr on treatment with $AgNO_3$ in aqueous alcohol.

Ph_5CrOH (5) is best prepared as follows:

$$Ph_5CrBr + KOH \xrightarrow[Et_2O]{dry} Kbr + Ph_5CrOH$$

It is golden orange, very slightly soluble in water, gives strongly alkaline solutions, absorbs CO_2, and replaces ammonia in ammonium salts. The hydroxide retains four mols of water over 33% KOH, two mols over $CaCl_2$, and becomes anhydrous over P_2O_5. If it is kept over P_2O_5 for a considerable period, there is a deep seated decomposition with the formation of diphenyl. Consequently, the structure is believed to be $Ph_5Cr(H_2O)_2OH.2H_2O$. When a dilute solution of the hydroxide in alcohol containing some water is partially precipitated with ether, the filtrate on drying over sulfuric acid gives an orange substance of the same composition as the dihydrate previously obtained over $CaCl_2$. However, this substance loses no water over P_2O_5.

Hein calls it "beta base", but offers no explanation for the differ-
ence in behavior. The dihydrate, tetrahydrate, and beta form all
melt quite sharply at 104-105°

In general the penta phenyl hydroxide reacts with acids or
salts (5,6) to form well crystallized compounds containing one less
phenyl group, though the same orange color is maintained. Study of
the reaction mechanism (7) has shown phenol and hydrogen to be the
by products. It is believed that the base must first solvate, then
rearrange and decompose. The hydrogen does not escape, but was
found, after considerable difficulty, to be attached to the
chromium of the salt (perhaps in the same manner as hydrogen on Pd).
The only property of the compound altered was the spectrum. Extens-
ive studies have yielded a few penta organo salts plus $(PH_5Cr)_2CO_3$.
$6H_2O$, $Ph_5CrHCO_3.3H_2O$, $(Ph_5Cr)_2SO_4.4H_2O$, and $Ph_5CrOAc.4H_2O$.

Many tetra phenyl salts have been prepared from Ph_5CrOH.
Ph_4CrI (5) is obtained when the pentaphenyl salt is treated with
excess HI in $CHCl_3$. The iodide is stable in the dark in vacuo and
forms addition compounds with $HgCl_2$ and AgI. A periodide, PH_4CrI_5,
may be obtained by treating a dilute alcoholic solution with an
excess of alcoholic iodine. The periodide shows no loss of iodine
on standing over 30% KOH in vacuo for several hours.

The perchlorate, Ph_4CrClO_4 (5), may be prepared by treating the
alcoholic base with an excess of aqueous perchloric acid. It is
unstable when dry, exploding in a few hours on warm days, on gentle
warming, or on slight percussion.

A simple tetra phenyl chromium compound, PH_4Cr, (8,9), was
deposited as a smooth copper red layer or orange-red crystals on the
cathode when Ph_4CrI was electrolyzed in liquid ammonia at -40 to
50°C.. It is quite unstable at room temperature, darkening and
evolving the odor of diphenyl after a short time. Freshly precipita-
ted, it dissolves completely in EtOH, changing quantitatively to
Ph_4CrOH. It does not have a metallic luster, form amalgams, or
give a blue solution in liquid ammonia. Its only metallic character-
istic is its strongly basic reaction with water.

Ph_4CrOH (5,10) has been prepared by the electrolysis of the
iodide in ethyl alchol and by treating the iodide with silver oxide.
It is obtained as the tri hydrate which loses one mole of water in
vacuo. This hydroxide gives the typical reactions of a strong base,
and in methyl alcohol is a stronger base then Ph_5CrOH. The halides
prepared from it proved identical with the halides previously pre-
pared.

The typically orange compound Ph_3CrOH (11) was obtained by
diluting the mother liquor after the separation of $(Ph_5Cr)_2CO_3.6H_2O$.
It is quite unstable in concentration solution, gives reactions
typical of solutions of bases, and is a stronger base than either of

the other polyphenyl bases. The triphenyl base is decolorized by H_2O_2 and very dilute $KMnO_4$.

$Ph_3CrI \cdot Et_2O$ (11) may be prepared by treating the aqueous triphenyl base with KI or HI. Its behavior is similar to that of the penta and tetra phenyl halides.

<u>Ph_3Cr</u> (10) can be prepared by the electrolysis of Ph_3Cr I in anhydrous liquid ammonia or by treating the iodide with a solution of sodium in liquid ammonia. This brownish yellow deposit is less stable than Ph_4Cr readily splitting off diphenyl. In air it is converted to Ph_3CrOH.

Since both brown Ph_2CrX and green PhCrO (1) have been identified among the decomposition products of the tri, tetra, and penta phenyl series of compounds, the phenyl series includes five types of compounds. They are as follows: Ph_5CrX, Ph_4CrX, Ph_3CrX, Ph_2CrX, and $PhCrX_2$.

III. Substituted Phenyl-Cr Compounds

An idea of the substituted phenyl compounds which have been prepared may be gained from the following table (12,13,14).

Tolyl	$p(CH_3-C_6H_4)_{5,4,3}CrX$, $o(CH_3-C_6H_4)_{5,4,3}CrX$
Xylyl	$1,3,4-[(CH_3)_2C_6H_3]_{5,4}CrX$
Naphthyl	$alpha(C_{10}H_7)_2CrBr$
p-Br phenyl	$p(Br-C_6H_4)_4CrBr$, $p(Br-C_6H_4-C_6H_4-C_6H_4)_5CrBr$
m-Cl phenyl	$m(Cl-C_6H_4-C_6H_4)_2Cr(C_6H_4)_{1,2}$ $Cr(C_6H_4-C_6H_4Cl)_{2,3}$

In working with the above compounds it has been found that the stability of the C-Cr bond depends to a large degree on the organic radical. Stability decreases with increasing saturation of the radical. The yield is very poor with the halogen substituted phenyl compounds where very complex mixtures are the chief product.

IV. Relation of Organo-Cr Compounds to the Complex Chemistry of Chromium

Hein and his coworkers studied the formation of organo-Cr compounds using many complex Cr compounds (1,15,16,17). The results of this work may be stated in the following general rule: Only those complex derivatives of $CrCl_3$ and $CrBr_3$ (probably also CrI_3) in which at least three halogens are connected directly (i.e. not ionizable) with Cr and do not contain any ions in the outer sphere permit the introduction of the organic radical in place of the halogen atoms.' It may be noted that this corroborates the assumption that $CrCl_3$ and $CrBr_3$ are unionized. A similar inference may be drawn from the fact that chromous salts such as $CrCl_2$ and $Cr(OAc)_2$ will also react with PhMgBr.

BIBLIOGRAPHY

1. F. Hein, J. Prakt. Chemie, 132, 59 (1931)
2. F. Hein, Ber., 52B, 195 (1919)
3. F. Hein, Ber., 54B, 1905 (1921)
4. F. Hein, J. Reschke, and F. Pintus, Ber., 60B, 749 (1927)
5. F. Hein, Ber., 54B, 2708 (1921)
6. F. Hein et al., Ber., 61B, 730 (1928)
7. F. Hein et al., Ber., 62B, 1151 (1929)
8. F. Hein and W. Eissner, Ber., 59B, 362 (1926)
9. F. Hein and E. Markert, Ber., 61B, 2255 (1928)
10. F. Hein and O. Schwartzkopf, Ber., 57B, 8 (1924)
11. F. Hein, Ber., 54B, 2727 (1921)
12. F. Hein and R. Spaete, Ber., 57B, 899- (1924)
13. F. Hein and R. Spaete, Ber., 59B, 751 (1926)
14. F. Hein and W. Retter, Ber., 71B, 1966 (1938)
15. F. Hein and F. Pintus, Ber., 60B, 2388 (1927)
16. F. Hein, J. Reschke and F. Pintus, Ber., 60B, 679 (1927)
17. F. Hein, Ber., J. Prakt. Chem. 153, 160 (1939)

Methods of Measuring Aqueous Vapor and Dissociation Pressures

Philip Faust

February 18, 1947

Practical and theoretical considerations have united to arouse interest in vapor pressure studies of hydrates. The earlier work was done in order to test Van't Hoff's equation and other thermodynamic laws for the case of salt hydrates. In addition, a knowledge of the exact conditions under which salts are efflorescant, stable or deliquescent depends on an accurate knowledge of the vapor pressure of hydrates.

Early Investigations

The work on vapor pressure studies which was done prior to 1875 has little scientific value. Between 1875 and 1881 several investigators discovered and formulated the fundamental fact that a mixture of two hydrates is necessary to produce a nonvariant system with a definite vapor pressure for each temperature.

In general, there are three types of methods for the determination of the vapor pressures of salt hydrates: static, dynamic and indirect.

1. Static Methods

The first involves the introduction of the hydrate into an ordinary barometer tube and recording the lowering of the mercury. This was used by Lescoeur (1) and Pareau (2).

Frowein (3) made some improvements. He had the pair of hydrates in one bulb, concentrated sulfuric in another and the two connected by a tube filled with olive oil.

Menzies (4) had used cottonseed oil as his liquid. The advantage of oils over mercury is that they give greater differences in height.

A scheme used by Lescoeur (1) consisted in determining the dew point of air above the hydrates.

2. Dynamic Methods

The first dynamic method was developed by Mueller-Erzbach (5) who assumed that the vapor pressures of two substances are proportional to the relative rates at which water vapor passed out of similar flasks containing the hydrates when the flasks were placed in a dessicator.

The method introduced by Tammann (6) consists in passing measured volume of air slowly through a tube containing the hydrate and calculating the vapor pressure from the loss in weight. Its results aren't satisfactory when equilibrium is reached slowly.

3. Indirect Methods

In these, the vapor pressure is determined by bringing the hydrate into equilibrium with some liquid whose aqueous vapor pressure is known.

Mueller-Erzbach (5) determined the concentration of sulfuric acid over which a pair of hydrates neither gained nor lost weight.

Lineberger (7) suggested obtaining equilibrium by shaking the hydrates with an excess of a liquid in which they were insoluble, but which would dissolve small amounts of water. He used ether and measured the water content by change in boiling point.

Foote and Scholes (8) used ethyl alcohol as a reference liquid and determined the water content by density measurements.

Factors Governing the Selection of Methods

The static methods are not very good for measuring the vapor pressure of hydrates.

First many solid hydrates approach equilibrium very slowly.
Second the equilibrium is ordinarily approached from one side only.
Third the presence of absorbed gases on the hydrate raises large errors.
Fourth no entirely satisfactory confining liquid is available.

The principal objections to the ordinary dynamic methods are similar to those for the static methods.

The indirect methods of shaking up with some anhydrous solvent offer the advantage of permitting the equilibrium to be approached from both sides.

Ether takes up such small amounts of water that its accurate determination is difficult and ethyl alcohol suffers from the opposite effect.

The answer to the above difficulties is to find a solvent intermediate in properties between the two just mentioned. One such solvent is iso-amyl alcohol, chosen by Wilson (9).

Several methods are proposed for determining the amount of water in the alcohol: the addition of Mg_3N_2 to liberate NH_3 which could be titrated, a colorimetric method using cobalt chloride, a conductivity method using cobalt chloride, and finally a conductivity method using potassium thiocyanate (10). This last method is the best.

One dynamic method

A dynamic method used by Bonnell and Burridge (11) consists in passing dry air over a salt hydrate, through phosphorus pentoxide tubes, through a water saturator and finally

through another phosphorus pentoxide tube. The vapor pressure can be calculated by the weights of water absorped. The apparatus for this is somewhat complicated.

Another Indirect method.

Collins and Menzies (12) have used the method of allowing sulfuric acid of known concentration to alter its own concentration until its aqueous pressure matches that of the material under investigation. This is a simple accurate method.

Collins and Menzies have attempted to explain earlier discrepancies and difficulties by saying there are not always just two crystalline and one vapor phase present. There may be a layer of non-vaporous water present on the surface of the "active points" (points where the two crystalline phases are in contact). This alters the phase rule prediction.

Menzies and Potter (13) found that dehydration of a hydrate may be more rapid and thorough in the presence of increased pressures of water vapor.

Below are some conclusions reached by Collins and Menzies in their work:

They found (1) that the difficulty due to this water layer at the "active points" becomes less apparent, the higher the temperature. (2) that material which has for purposes of measurement, previously been in contact with a higher pressure of water vapor at a higher temperature is prone to yield pressure values which are too high in comparison lower temperature measurements which immediately succeed them. (3) that in certain cases, a genuine equilibrium pressure appears to present itself in experiments of customary duration, which falls in value only slowly with time. (4) that with different hydrate pairs, the abnormality is the greater the lower the dissociation pressure for the same temperature. (5) that, if the material for investigation must be prepared by efflorescence, discrepancies are best avoided by preventing undue access of water vapor to the material prior to measurements.

References

1. Lescoeur, Ann. chim. phys. 6 16 378 (1889), 21 511 (1890).
2. Perreau, Wied. ann. 1 55 (1877).
3. Frowein, Z. physik chem. 1 5, 362 (1887).
4. Menzies, J. Am. Chem. Soc. 42 1951 (1920).
5. Mueller-Erzbach, Ber. 14 1093 (1881).
6. Tammann, Ann. chim. phys. 63 16 (1897).
7. Linebarger, Z physik Chem. 13 500 (1894).
8. Foote and Scholes, J. Am. Chem. Soc. 33 1309 (1911).
9. Wilson, ibid. 43 704 (1921).
0. Noyes and Westbrook, ibid 43 726 (1921).
1. Bonnell and Burridge, Trans. Faraday Soc. 31 473 (1935)
2. Collins and Menzies, J. Phys. Chem. 40 379 (1936).
3. Menzies and Potter, J. Am. Chem. Soc. 34 1452 (1912).

SULFUR MONOXIDE

J. B. McPherson, Jr.

February 25, 1947

I. Introduction

Sulfur monoxide was first described in 1883 by Heumann (1), who observed a faint white phosphorescence and peculiar odor on heating sulfur to 200°C. in the dark and in the presence of air. He named the compound formed sulfur monoxide since it showed a sulfur-oxygen ratio of one to one.

Since that time its existence has been suggested in the postulated mechanism of several known reactions.

For example, the presence of pentathionic acid in "Wackenroder's solution" was explained by the following equations: (2)

$$1.\ SO_2 + H_2S \longrightarrow SO + H_2O + S$$
$$2.\ H_2O + 5SO \longrightarrow H_2S_5O_6$$

It was also proposed that the decomposition of thiosulfuric acid proceeds thus: (3)

$$H_2S_2O_3 \longrightarrow 2SO + H_2O$$

Several early attempts were made to prepare sulfur monoxide, but at that time they were unsuccessful. Dienes and Elstner (4) and later Gruner (5) obtained only sulfur dioxide, sodium sulfite and sodium thiosulfate upon heating sodium hyposulfite. The latter author also tried the action of thionyl chloride on silver, magnesium, sodium and stannous chloride. Staudinger and Kreis (6) attempted to prepare it from the thermal decomposition of thionyl bromide.

A significant observation was made in 1929 by Henri and Wolff (7). They reported the formation of a new emission spectrum in the range of 2500 to 3900 Å, when sulfur dioxide was subjected to an alternating electric discharge under reduced pressure. Their calculation of the dissociation energy of sulfur monoxide into sulfur and oxygen gave a value one half that for the dissociation of sulfur dioxide. Thus the new spectrum was attributed to sulfur monoxide.

II. Methods of Preparation

Schenk (8) succeeded in isolating sulfur monoxide by exposing a mixture of sulfur dioxide and sulfur vapor to an electric discharge at a pressure of about 0.5 mm. Hg. The following reactions were given to show its formation:

$$SO_2 + S \longrightarrow 2SO$$
$$2SO_2 \longrightarrow 2SO + O_2.$$

The sulfur monoxide was detected by its absorption spectrum which was found to lie in approximately the same range as the emission spectrum.

Schenk and Platz (9) obtained sulfur monoxide by heating silver, sodium, antimony, tin or stannous chloride with thionyl chloride in accordance with the reaction

$$SOCl_2 + 2M \longrightarrow 2MCl + SO.$$

Thermal decomposition of thionly halides, preferably the bromide, proved successful for Schenk and Triebel (10). More recent preparative methods include the slow oxidation of hydrogen sulfide (9,11,12) or carbon disulfide (17,18) with oxygen and the photochemical decomposition of sulfur dioxide (13). But the best methods remain the reaction of sulfur dioxide and sulfur vapor in an electric discharge, and the reduction of thionyl chloride with a metal. Schenk (3) gave convenient directions for these in a review article. He has also given directions for a method involving the direct combination of sulfur and oxygen (3,10)

$$1/2\ S_2 + 1/2\ O_2 \longrightarrow SO.$$

III. Physical Properties

There has been some disagreement concerning the molecular weight of gaseous sulfur monoxide, however it is now generally accepted that it exists as a dimer S_2O_2.

Kondrat'eva and Kondrat'ev(14) found that the absorption spectrum calculated from the known emission specturm differed from the known absorption spectrum, indicating that the absorption carrier must be S_2O_2 rather than SO. Schenk (15) however claimed that they had misinterpreted their data and believed the gas to be monomeric. This contradicted his own earlier statement that sulfur monoxide was a mixture in which approximately 64% of the gas was associated as a dimer.

Jakovleva and Kondrat'ev (13) reported that under the conditions of their experiment only S_2O_2, and not SO, could be formed from the photochemical decomposition of sulfur dioxide.

Sulfur monoxide gas condenses on cooling in a liquid air bath to an orange-red solid which is soluble in carbon tetrachloride (19). The molecular weight of the dissolved product varies from 300 to 800.

The most important property of sulfur monoxide from a research standpoint is its absorption spectrum, which makes possible the detection of SO even in extreme dilution. There has been disagreement on the carrier of this absorption, which in general paralleled the molecular weight controversy.

Cordes (20) believed the carrier to be a metastable S_2 molecule. But most investigators (13,14,21) consider the carrier to be S_2O_2.

IV. Chemical Properties

Gaseous sulfur monoxide is stable to decomposition at room temperatures and at low pressures. It decomposes to sulfur and sulfur dioxide on increasing the pressure and temperature. (22, 23, 24)

The above-mentioned condensed form is thought to be a poly sulfur oxide with a variable sulfur-oxygen ration of 2-4:1 (3,19). The solid decomposes to sulfur dioxide and sulfur on warming. It shows many of the reactions of sulfur monoxide gas and is thought to contain SO units in a polymeric chain.

The gaseous form is decomposed readily to sulfur and sulfur dioxide by silica gel (23,26), silver sulfide (25) and on warming with activated charcoal (23).

Thionyl chloride or bromide is obtained by treating SO with the appropriate halogen (3,27).

It does not react with rubber (23) or ethylene (3). B. S. Rao (28) reported the dehydrogenation of liquid paraffin or decalin as well as methanol and ethanol with the liberation of hydrogen sulfide. The following reaction was suggested:

$$2SO + CH_3OH \longrightarrow H_2S + HCHO + SO_2.$$

Sulfur monoxide is stable with oxygen (24) and with nitric oxide (27,29) at room temperature and low pressure. However at increased temperature and pressure it reacts with oxygen to give sulfur, sulfur dioxide and sulfur trioxide. (30, 31, 32)

Wilkins and Soper (29,33) have studied the effect of sulfur monoxide on nitrous acid, nitric acid and nitrosylsulfuric acid. On passing SO through either HNO_2 or HNO_3 solutions, nitrogen is evolved in accordance with the following equation:

$$3SO + N_2O_3 \longrightarrow 3SO_2 + N_2.$$

With nitrosylsulfuric acid, nitric oxide rather than nitrogen is evolved.

Sulfur monoxide reacts with water to give hydrogen sulfide, sulfurous acid and polythionic acids. (3) Thiosulfites, sulfites and sulfides are formed when it is passed into a basic solution

$$3SO + H_2O \longrightarrow H_2S + 2H_2SO_3$$
$$S_2O_2 + H_2O \longrightarrow H_2S_2O_3.$$

Stamm and Wiebusch (39) recently reported the oxidation of hydrogen iodide to free iodine in a carbon tetrachloride solution by sulfur monoxide.

V. Uses

The main use of sulfur monoxide remains that of a research tool in proving reaction mechanisms. Emanuel, Semenov, and Pavlov (12,34,35,36,37,38) have recently made an extensive study of the oxidation of hydrogen sulfide with oxygen in which sulfur monoxide has been shown to be an intermediate product.

BIBLIOGRAPHY

1. K. Heumann, Ber., 16 139 (1883)
2. Fritz Ephraim, "Inorganic Chemistry", Nordeman Publishing Co. Inc., New York, 1943, 4th ed. rev., p. 562.
3. P. W. Schenk, Chem. Ztg., 67 251, 273 (1943)
4. O. von Dienes and G. Elstner, Z. anorg. allgem. Chem., 191, 340 (1930).
5. E. Gruner, ibid, 212, 393 (1933)
6. H. Staudinger and W. Kreis, Helv. Chim. Acta, 8, 71 (1925)
7. V. Henri and F. Wolff, J. Phys. et Rad., 10, 81 (1929)
8. P. W. Schenk, Z. anorg. allgem. Chem., 211, 150 (1933)
9. P. W. Schenk and H. Platz, ibid, 215, 113 (1933)
10. P. W. Schenk and H. Triebel, ibid, 229, 305 (1936)
11. N. M. Emanuel, Bull. acad. sci. U.R.S.S., Classe sci. chim., 1942, 221.
12. N. M. Emanuel, D. S. Pavlov, N. N. Semenov, Compt. rend. acad. sci. U.R.S.S. 28 618 (1940).
13. A. Jakovleva and V. Kondrat'ev, Acta Physicochim. U.R.S.S., 13, 241 (1940).
14. E. Kondrat'eva and V. Kondrat'ev, J. Phys. Chem. (U.S.S.R.), 14, 1528 (1940)
15. P. W. Schenk, Z. Physik, Chem., B52, 295 (1942)
16. P. W. Schenk, Z. anorg. allgem. Chem. 222, 177 (1935)
17. P. W. Schenk, ibid, 220, 268 (1934)
18. V. Kondrat'ev, Bull. acad. sci. U.R.S.S., Classe sci. chim., 1940, 501
19. P. W. Schenk, Z. Elektrochem., 47, 855 (1941)
20. H. Cordes, Z. Physik., 105, 251 (1937)
21. P. W. Schenk, Z. Physik. Chem., B51, 113 (1942)
22. C. W. Montgomery and G. S. Kassel, J. Chem. Phys., 2, 417 (1934)
23. H. Cordes and P. W. Schenk, Trans. Faraday Soc., 30, 51 (1934)
24. H. Cordes and P. W. Schenk, Z. Electrochem., 39, 594 (1933)
25. B. S. Rao and M. R. Rao, Current Sci., 12, 323 (1935)
26. H. Cordes and P. W. Schenk, Z. anorg. allgem. Chem., 214, 33 (1933)
27. P. W. Schenk, ibid, 233, No. 4, 385 (1937)
28. B. S. Rao and M. R. Rao, Current Sci., 4, 406 (1935)
29. C. J. Wilkins, J. Chem. Soc., 1940, 1157
30. E. Kondrat'eva and V. Kondrat'ev, Compt. rend. acad. sci. U.R.S.S., 31, 128 (1941)
31. E. Kondrat'eva and V. Kondrat'ev, J. Phys. Chem. (U.S.S.R.), 15, 731 (1942)
32. E. Kondrat'eva and V. Knodrat'ev, ibid, 18, 102 (1944)
33. C. J. Wilkins and F. G. Soper, J. Chem. Soc., 1939, 600
34. N. N. Semenov and N. M. Emanuel, Compt. rend. acad. sci. U.R.S.S., 28, 219 (1940).
35. N. N. Semenov, ibid, 36, 145 (1942)

36. D. A. Pavlov, N. N. Semenov, N. M. Emanuel, Bull. acad. sci. U.R.S.S., Classe sci. chim., 1942, 98
37. N. M. Emanuel, J. Phys. Chem. (U.S.S.R.), 19, 15 (1945)
38. N. N. Semenov, Bull. acad. sci. U.R.S.S., Classe sci. chim., 1945, 210
39. H. Stamm, K. D. Wiebusch, Naturwissenschaften, 32, 42 (1944)

Miscellaneous References

H. M. Hulbert, J. O. Hirschfelder, J. Chem. Phys., 9, 61 (1941)
H. Lessheim, R. Samuel, Phil. Mag., 25, 667 (1938)
R. Chereton, Bull. soc. roy. sci. Liege, 11, 54 (1942)
N. M. Emanuel, Compt rend. acad. sci., U.R.S.S., 5, 250 (1942)
K. K. Kelley, U.S. Bur. Mines Bull., No. 406, 16 (1937)
C. E. H. Bawn, J. Chem. Soc., 1933, 145

Crystal Chemistry

A. R. Matheson

March 4, 1947

I. INTRODUCTION

Stillwell (27) defines crystal chemistry as "the study of (1) the laws governing the arrangements of atoms in solids and (2) the influence of the arrangement and the electronic structure of the atoms upon physical and chemical properties of the solid". Books by Stilwell (27), Pauling (19), Wells (31), and Davey (4) deal with various phases of crystal chemistry and with the more precise and complex phases of the subject.

The study of crystals began over 150 years ago, but until the beginning of the 20th century no hypotheses were brought forward explaining the interior arrangment of crystals. Barlow (1) and Bollas (26) visualized atoms as spheres and having certain arrangements in crystals. The use in 1912 of x-rays to produce a diffraction pattern of a crystal w s a major advance in the development of atomic structure knowledge. However, not until the work of Goldschmidt (6,7,8,9,) and Pauling (16,17,18) during the 1920's was there any real correlation between size and properties of materials. Stillwell consideres this work by Goldschmidt and Pauling as the beginning of crystal chemistry.

II. ATOMIC SIZE

The size of atoms or ions is important in determining the structure of the elements or compounds, or vice versa, and this size relationship is in turn manifested in certain determinable physical values.

The concept of atoms or ions being definite, more or less solid, spheres was used in early discussions of atomic size, but with the advent of wave mechanics this viewpoint is no longer considered accurate. While we speak of atomic and ionic radii these are used only in a relative manner and it is realized the values obtained for the various radii are dependent upon the method of measurment, the nature of the association of the atom with other atoms, the fundemental constants used, and assumptions of some "base" atom's dimensions. Distinction must be made in particular as to the conditions of the application of the terms atomic and ionic radii. Pauling (19) gives the limits of accuracy for the three main methods of determining radii as, (a) spectroscopic-0.01-0.001 A.U.; (b) electron diffraction of gases - 0.01-0.05 A.U.; X-ray diffraction of gases-0.1-0.2 A.U.; (c) X-ray analysis- 0.001 A.U..

III. ATOMIC RADII

Interatomic distances may be divided into two main classes, covalent and ionic. Distances in covalent compounds may be used in the determination of atomic radii and such radii agree with the radii of the same atoms as found in the elemental forms. Huggins (10) published a series of articles containing the first tabulations of atomic radii values for a series of elements for use in crystals containing homopolar or electron-pair bonds. Huggins used the method reported by Bragg (2) whereby the interatomic distances for the alkali halides are tabulated and the differences in values between the horizontal and vertical members in a series are listed. A constant difference is found as you change either the metal or the halide. This constant-difference

value may be used to compute the interatomic distance in some other compound. Huggins used the oxides, sulfides, selenides and tellurides of zinc, cadmium and mercury for the determination of the atomic radii of some 19 elements. The radii of carbon, silicon, germanium, and gray tin were taken as half the interatomic distance in crystals of these elements. He further used a sulfur radius of 1.04Å. The tetrahedral structure was proposed for zinc, cadmium, divalent mercury and monovalent copper in combination with the group VIB elements.

In 1926 he revised his earlier works because the additivity rule, whereby the radii of two atoms are added together to obtain their interatomic distance in a compound, was found not to be correct under all conditions of use, and secondly, as shown by Wyckoff (32), the concept of constant radii for any one atom in a wide series of compounds was no longer valid.

The next comprehensive piece of work on covalent radii was in 1934 by Pauling and Huggins (20). They discuss the covalent bond from a quantum mechanical standpoint. From their calculations they show the formation of the new common dsp^2 and d^2sp^3 bonds as well as the strength of these bonds. The dsp^2 bonds are found in bivalent nickel, palladium and platinum compounds where there are eight electrons in the outer d shell. When these electrons are placed two in an orbit there is one d orbit left to form a bond through combination with the sp^3 orbitals of the next outer shell. Four strong orbitals can be formed in this manner and have been found to be directed towards the corner of a square, hence are called square bond orbitals. For six or less d electrons there are two d orbits available for bond formation, which in combination with s, p_x, p_y, and p_z are found to give six equivalent d^2sp^3 orbitals directed towards the corners of a regular octahedron. An additional six-bond type is formed with the orbitals somewhat unsymmetrical and directed towards the corners of a trigonal prism. The bond strength here is the strongest of all the covalent bond types.

The tetrahedral form on bonding occurs when the tetrahedral orbitals sp^3 are used. These bonds form at an angle of 109° 28' with each other and justify the tetrahedral carbon atom and other tetrahedral atoms.

Thus we may classify atomic radii upon the above basis into tetrahedral, normal valence, octahedral, trigonal and square types.

Many of the values listed by Pauling and Huggins for the tetrahedral and normal covalent radii are the same as given by Huggins in his earlier papers. In general the additivity rule was found to hold for the values they give, and they did not believe the partial ionic character of a bond would cause too much of the deviation observed in certain interatomic distances.

For normal valence compounds of non-metallic atoms each atom forms a number of covalent bonds equivalent to its valence. The normal valence values for carbon, silicon, germanium and tin are the same as for tetrahedral crystals since the tetrahedral crystal is the normal form of these elements. For those elements capable of forming multiple bonds the radii are found to decrease as the number of bonds increases.

Octahedral radii are found mainly in transition elements

such as group VIII, but also include tin, lead, selenium and tellurium in the quadrivalent state. For the group VIII elements the bonds are d^2sp^3 type, whereas for elements like tin they are the sp^3d^2 type. The octahedral form of a crystal is usually of the pyrite form of structure. The octahedral form of a crystal is usually of the pyrite form of structure. The octahedral radius of iron for example can be calculated by subtracting the tetrahedral radium of sulfur from the Fe-S distance observed within the crystal.

The trigonal prism is found only in MoS_2 and WS_2, where the metal atom is surrounded by six sulfur atoms at the corners of a trigonal prism.

Square radii are found in compounds such as K_2PdCl_4 and K_2PtCl_4 where the Pd or Pt atom is surrounded by four chlorine atoms at the corners of a square. For group VIII elements the square radii are the same as the octahedral radii for the same elements.

In 1941 Schomaker and Stevenson (24) proposed certain revisions for the work of Pauling and Huggins in computing atomic radii. From more recent measurements on interatomic distances in F_2 (25), H_2O_2, and N_2H_4 they believed the covalent single bond radii of F, O, and N should be increased in value. They also found it necessary to apply a correction which would account for the partial ionic character of various bonds. The length r_{ab} between two atoms with normal covalent radii r_a and r_b, and electronegativities x_a and x_b, is given by

$$r_{ab} = r_a + r_b - B(x_a - x_b). \quad B = 0.09$$

The expression $-B(x_a-x_b)$ is associated with the extra ionic character of the bond A-B.

V. IONIC RADII

Bragg (2) made one of the first tabulations of ionic radii using x-ray data in his calculations. The absolute value used by Bragg as a reference value was later proven inaccurate and he did not realize the possibility of variation in ionic radii in different compounds of the same element.

The major advances in ionic radii determinations have been made by Wasastjerna (30), Goldschmidt (6,7,8,9), Pauling (16,17, 18,21), and Zachariasen (33).

Wasastjerna calculated a number of ionic radii from optical relationships within the molecule and his values of 1.33 Å for F^- and 1.32 Å for $O^=$ were later used as absolute values by Goldschmidt.

Goldschmidt during the 1920's published a great series of articles upon the geochemical laws of distribution and crystal structure. As a result of his experiments and using the above values of Wasastjerna for fluorine and oxygen, by empirical means he calculated the radii of a large number of ions: being careful to use only crystals considered to be essentially ionic in nature.

In 1927 Pauling (16) published a set of ionic radii calculated from wave mechanics relationships between ions. His values agreed reasonably well with those of Goldschmidt and served to establish a firm basis for crystal chemistry. From the atom con-

sidered by Pauling we no longer find the concept of a solid sphere, but a nucleus surrounded by a cloud of electrons. The atom is considered to be spherically symmetrical, with electron density greatest at the nucleus and decreasing exponentially as r, the distance from the nucleus, increases. The electrons in the outer shell of the atom are considered to have the greatest influence of the inner electrons upon the positive charge, Ze, where Z is the atomic number and e the charge upon the electron, is known as the screening effect, Se. The effective nuclear charge which determines the attraction exerted upon the outer electrons is given by (Z-S)e. Tables of screening constants, S, are given by Pauling (18,21). The radii are obtained by dividing the observed interionic distance of a compound in the inverse ratio of the effective nuclear charge. The univalent radii obtained in this manner represent the relative extension in space of the outer electron shells and may be considered the relative sizes of the ions. These univalent radii are the ones which when added together reproduce the observed interionic distances in the crystal, if the crystal is of the NaCl type. For multivalent ions it is necessary to apply a correction factor.

Zachariasen (33) calculated a set of univalent radii which parallel in most cases those of Pauling. Zachariasen made corrections for coordination number, coulombic or valence forces, and radius ratio effects.

Thus we see that the interactions between an ion and its neighbors are what largely determine the equilbrium interionic distances in ionic crystals. Radii have been determined for ions which radii when added together give the distances between the ions in a compound. The effective size of an ion is not constant and varies with coordination number, valence forces, and the ratio of the cation and anion radii. For proof that certain compounds possess ionic bonding, and thus have ionic radii, Friedman and Shuler (5) offer seven proofs to be applied.

V. SIZE RELATIONSHIPS TO PROPERTIES OF MATTER

An important property of the elements is atomic volume which may be obtained by dividing the atomic weight of the element by its density in the solid state. If atomic volume values are plotted against increasing atomic number a curve is obtained which closely parallels a curve of atomic radii plotted against increasing atomic number. Moeller (14) has plotted the atomic volume of the elements going across the periodic table and obtained a series of curves sloping towards the middle of the table from both ends of a series. When atomic volumes are calculated for some other state besides the solid state an error is introduced.

In group IIIA an interesting relationship is observed in the atomic volume values. From scandium to lanthum there is the expected increase in atomic radii and atomic volume, but in going from lanthanum to lutecium there is a general decrease in atomic radii and atomic volume. Klemm and Bommer (12) examined the atomic volumes of the rare earth metals and found excessively large volumes for europium and ytterbium which they explain as probably due to the fact that these two elements crystallize in the cubic system, whereas, the other rare earths crystallize in the hexagonal system. Deviations from the curve by several elements is attributed to the formation of ionization states within the metal by the element in question. The metals in general show the lanthanide contraction effect, but to a lesser degree than is shown in the oxides.

If we consider the molecular size relationships among compounds of these elements we find a somewhat similar relationship as with atomic volumes. The size of an ion is larger or smaller than the size of its parent element depending upon whether electrons have been gained or lost in the ionization process. For two adjacent positive ions in a horizontal series the ions are isoelectronic but the increase in nuclear charge Z, causes a decrease in size as the atomic number increases. In the rare earth series we do not obtain an isoelectronic series as the atomic number increases still a decrease is noted in the ionic radii of the ions. While the outer electronic structure remains the same additional electrons are added into the 4f shell but fail to nullify the increased nuclear charge and a decrease in size is noted. Grimm is reported (15) to have predicted such a decrease in size among the rare earths and also a parallel decrease in molecular volume and basicity.

Goldschmidt (7,9) was the first to clearly show the decrease in size in the rare earth oxides and to realize the effect of such a contraction upon the elements immediately following the rare earths. From x-ray data lattice constants were obtained for the various oxides and when these lattice constants were plotted against increasing atomic number a regular decrease was noted. Goldschmidt called this decrease in size the "lanthanide contraction". Molecular volumes of the octahydrated sulfates of the rare earths show a corresponding decrease in value with increasing atomic number (15).

From these volume relationships Goldschmidt calculated the ionic radii which we have discussed above. Here again we find an increase in ionic radius from scandium to lanthanum, but a decrease from lanthanum to lutecium.

A large cation would be expected to have less attraction for electrons or anions than one of smaller size, and if basicity is considered as a function of the relative ease with which electrons or anions are held or given up, we would then expect a decrease in basicity with a decrease in cation size. If we consider the rare earths we find that we have a decrease in basicity with increasing atomic number, but with decreasing ionic size, thus we have lutecium hydroxide less basic than lanthanum hydroxide.

To more precisely consider the effects of both charge and size upon basicity Cartledge (15) used the relationship $\emptyset = \frac{\text{cation charge}}{\text{cation radius}}$, where a hydroxide will be basic, amphoteric, or acidic as the square root of $\emptyset$ is less than 2.2, between 2.2 and 3.2, or greater than 3.2 respectively. Sun (28) recalculated the values given by Cartledge. By using more accurate ionic radii Sun found that a hydroxide was basic, amphoteric, or acidic as $\emptyset$ varied from below six, around six, and above six respectively. Sun and Li (15) used the relationship AV/n^3, where A is atomic number, V the valence, and n the principal quantum number of the highest quantum level in the neutral atom. There standard values were, less than 1.44, around 1.44, and greater than 1.44 for basic, amphoteric, and acidic behavior. Any of these calculations may be used an still show the relative decrease in basicity of the rare earth series with increasing atomic number.

Other effects of the lanthanide contraction are apparent in the elements which immediately follow the rare earths. As

a result of the lanthanide contraction the chemical properties of pairs of elements such as Zr-Hf, Mo-W, Cb-Ta, etc. are very similar and it is difficult to separate them. Physical properties also show this similarity. For example, in the titanium group

At. No.	Compound	Density	Molecular volume
22	TiO_2	4.20	18.8
40	ZrO_2	5.73	21.5
72	HfO_2	9.68	21.7

If, as has been recently proposed, we have a second rare earth series designated as the actinide series (25), from analogy we should also expect an "actinide contraction". Considerable evidence (3,13,22,25,290) has been accumulated in the literature to show the resemblance between the rare earths and the transuranic elements. Quill (22) states that there should be a "shrinkage in atomic and ionic sizes of these elements (transuranic) analogous to the 'lanthanide contraction' in the rare earth group". At the time however, he was considering a group of elements of atomic number 95 to 108. There is insufficient data available to verify such an expectation, but a decrease in size of atomic volume is noted between thorium and uranium (15).

Thus we have seen a few of the many unique properties of matter which may be explained in terms of the size of atoms.

References

. Barlow, W., Scientific Proc. Royal Dublin Soc., 8, 527 (1893-1898).
. Bragg, W. L., Phil. Mag., 40, 169 (1920).
. Curie, I., and Savitch, P., Compt. Rend. 206 906 (1938)
. Davey, W. P., A Study of Crystal Structure and Its Applications, McGraw-Hill, (1934) Chap XIII.
Friedman, H. B. and Shuler, K. E., J. Chem. Educ., 24, 11 (1947).
Goldschmidt, V. M., Skrifter Norske Videnskap. Akad. Oslo, I., Math.-Nat. Kl. (1926) No. 7; Trans. Faraday Soc. 25,253 (1929).
Goldschmidt, V. M., Barth, T, and Lunde, G., Skrifter Norske Videnskap. Akad. Oslo, I, Math.-Nat. Kl. (1925) No. 7.
Goldschmidt, V. M., and Thomassen, L., Videnskap.-Skrifter, I, Math. Nat. Kl. Kristiana, (1924) No. 5.
Goldschmidt, V. M., Ulrich, F, and Barth T., Skrifter Norske Videnskap. Akad. Oslo, I, Math. Nat. Kl. (1925) No. 5.
Huggins, M. L., Phys. Rev., Ser. 2, 19, 246 (1922); ibid, 21, 205, 211, 379, 509, (1923); ibid., 26, 1086 (1926).
Hume-Rothery, W. Phil. Mag. 10, 217 (1930).
Klemm, H., and Bommer, H., Z. anorg. Chem., 231, 138 (1937).
McMillan, E. and Abelson, P., Phys. Rev., Ser. 2, 57, 1185 (1940).
Moeller, T., J. Chem. Educ., 17, 44 (1940).
Moeller, T., and Kremers, H., Chem. Rev., 37, 97 (1945).
Pauling, L., J. Am. Chem. Soc., 49, 965 (1927).
Pauling, L., ibid., 50 1036 (1928).
Pauling, L., Proc. Roy. Soc. (London) A, 114, 187 (1927).
Pauling, L., The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca, N.Y., (1945), 2nd Ed., Chaps. V and X.
Pauling, L., and Huggins, M. L., Z. Krist., 87, 205 (1934) (in English).
Pauling, L., and Sherman, J., ibid, 81, 1 (1932) (in English).
Quill, L. L., Chem. Rev., 23, 87 (1938).
Rogers, M. T., Schomaker, V., and Stevenson, D. P., J. Am. Chem. Soc., 63, 2610 (1941).

4. Schomaker, V., and Stevenson, D. P., ibid., 63, 37 (1941).
5. Seaborg, G., Chem. Eng. News., 23, 2190 (1945); ibid., 24, 1193 (1946); ibid., 25, 358 (1947).
6. Sollas, W. J., Proc. Roy. Soc. (London), 63, 270, 286 (1898); ibid., 26, 286 (1899).
7. Stillwell, C. W., Crystal Chemistry, McGraw-Hill, (1938) Chaps. II and III.
8. Sun, C. E., J. Chinese Chem. Soc., 5, 148 (1937).
9. Villar, G. E., C.A. 34, 3550 (1940); Ann. acad. brasil. Sci., 12, 51 (1940); J. Chem. Educ., 19, 286, 329 (1942); ibid., 21, 25 (1944).
0. Wasastjerna, J. A., Soc. Sci. Fennica, Comm. Phys. Math. I, (1923) No. 38.
1. Wells, A. F., Structural Inorganic Chemistry, Clarendon Press, Oxford, (1945), Chap. III.
2. Wyckoff, R.W.G., Proc. Natl. Acad. Sci., 9, 33, (1923).
3. Zachariasen, W, Z. Krist., 80, 136 (1931) (in English).

rting with line 5, page 80 should read: -
e electrons in the outer shell of the atom are considered to have greatest influence upon the size of the atom or ion. However, inner electrons absorb a large portion of the charge of the leus before it can reach the outer electrons. This influence of inner electrons upon the positive charge, Ze, where Z is the atomic ber and e the charge upon the electron, is known as the screening ect, Se.

THE POISONING OF CONTACT CATALYSTS

J. C. Richards

March 11, 1947

I. HISTORICAL

The investigation of the poisoning of catalytic reactions has been of considerable theoretical and technical importance since the days when contact catalysis was first discovered. As early as 1833, Faraday, recognizing the importance of poisoning in catalytic reactions, stated that "the only essential condition (for the reaction to take place) appears to be a perfectly clean and metallic surface". However, it was not until the 1920's that a real understanding of the catalytic reaction, and of the poisoning of that reaction, was obtained.

II. TECHNICAL IMPORTANCE

Two factors are responsible for the emphasis which is placed on poisons in industrial practice. The first is the high cost of almost all contact catalysts, and the second is the fact that extremely minute quantities of any of a variety of materials are sufficient to deactivate almost completely the ordinary contact catalyst. Inability to remove the last traces of poisonous materials from the reactants will spell the failure of any industrial catalytic process; for example, the "modern" contact process for sulfuric acid was patented in 1831 and attempts were made to put it into practice shortly thereafter, but the operators were unable to cope with the problem of poisoning of the platinum catalyst.

III. TYPES OF POISONS

Catalyst poisons may be divided into two categories, temporary and permanent. Temporary poisons are those which may be removed under the conditions of the reaction merely by excluding them from the reactants and running the system for a few minutes. An example of this type is water vapor in the synthesis of ammonia over an iron catalyst. In this reaction, no difficulty is experienced unless the partial pressure of the water vapor is allowed to become too high in the reaction mixture.

Permanent poisons are those which cannot be removed from the catalyst under the conditions of the reaction, and in fact usually can be removed only under drastic conditions. While most temporary poisons are merely preferentially adsorbed on the catalytic surface, permanent poisons form stable compounds with the catalyst. The best known examples of permanent poisons are the sulfides.

V. ADSORPTION AND CATALYSIS

Two types of adsorption may take place on the surface of a catalyst, van der Waals adsorption, and activated adsorption. (chemisorption). The former, a physical process with a heat of adsorption corresponding to the heat of liquifaction of the gas, does not lead to any catalytic activity. The latter, on the other hand, is a chemical process with a high heat of adsorption and does often lead to catalytic activity. The fact that adsorption alone is not enough to cause catalysis has been demonstrated by numerous investigators, among them Pease (1) and Maxted and

oon (2). Both of these papers showed for different systems that ne addition of enough poison to deactivate the catalyst had little ffect on its total adsorptive capacity. This obviously means that lthough the power of adsorption is common to a large part of the atalyst's surface, the actual catalytic activity is limited to a mall part of this total surface.

A quantitative determination of the ratio of active to inctive atoms in the surface of a promoted iron catalyst was made by mquist and Black (3). By measuring the amount of oxygen needed poison the catalyst for the ammonia synthesis, they were able calculate that only one surface atom out of 200 was catalytically tive.

DISTRIBUTION OF ACTIVITY OVER THE CATALYST SURFACE

Most of our knowledge about the distribution of activity among e active centers has come from studies of the effect of poisons varying amounts on a number of common catalysts. This variation activity is taken advantage of in the use of selective poisong to limit undesirable reactions without affecting the main retion. This may be accomplished in many cases by adding a material ich will react only with the most active centers on the catalyst rface without interfering with the less active ones. An exllent example of this is the treatment of a nickel catalyst with ckel ion to prevent ring hydrogenation in the catalytic reduction nitrobenzene to aniline (4). In a better known example, water added during the dehydrogenation of alconols to aldehydes in der to prevent further reactions of the latter.

The data presented thus far have demonstrated that there is very definite distribution of activity among the active centers a contact catalyst, but have not indicated what type of distrition is involved. A series of experiments by Maxted (5 & 6) and xted and Morrish (7) demonstrated rather conclusively that the tive centers of a platinum catalyst can be classified in two or haps three groups, the members of each group all having approxiely the same degree of activity. The evidence for this consion was based on the fact that a plot of catalyst activity vs. unt of poison on the catalyst yielded straight line graphs with , and in some cases two, inflection points. The straight line tions represent the adsorption of the poison on the most active up of centers, and the inflections indicate saturation of this up and the start of poison addition to the set of next lower ivity.

CHEMICAL STRUCTURE vs. TOXICITY

In efforts to obtain further indirect information about the racter of a catalytic surface, Maxted together with Evans, Mars and Morrish conducted a series of investigations aimed at relating chemical structure with toxicity (7-13). Their experits were all carried out by measuring the effect of the poison the rate of hydrogenation of crotonic acid in glacial acetic d over a platinum catalyst. The activity of the poison was luated by calculating the "poisoning coefficient" a from the lowing equation:

$$K_c = K_o(1-ac)$$

c = concentration of poison
K_o = rate of unpoisoned reaction
K_c = rate of poisoned reaction

This equation fits the straight-line plot of rate vs. quantity o' poison until the first inflection in the curve, which usually i found at about 50% of the original rate.

The first compounds investigated were sulfides, thiols, disulfides, and dithiols. The following conclusions were drawn:

1. Alkyl sulfides and thiols- Toxicity per unit of sulfr increased with increasing chain length. The rate of increase iclined as chain length increased
2. The ratio of toxicities of alkyl thiols to the corresonding dialkyl sulfides was 1 / 2.5, regardless of chain length
3. Addition of a second thiol group at the far end of e hydrocarbon chain decreased the toxicity, presumably by deeasing the mobility of the chain.
4. Disulfides were only slightly more toxic than corresonding monosulfides
5. Chain branching cut down the toxicity slightly; inoduction of a terminal double bond had little or no effect

The next group of compounds tested was made up of the hydrides phosphorous, arsenic, antimony and bismuth. The toxicities of e first three were approximately equal; that of bismuth was onelird higher than the others, probably because of its larger size.

I. SHIELDED DERIVATIVES OF TOXIC ELEMENTS

Some derivatives of phosphorous, selenium, tellurium, and fur were tested for toxicity under the same conditions as those lined above. The results are tabulated below:

TOXIC	NON-TOXIC
sulfide sulfite tetrathionate	sulfate sulfonate
phosphite hypophosphite	phosphate
tellurite	tellurate
selenite	selenate

It may be noted that the toxic derivatives all contain her unshared electron pairs or pairs shared with hydrogen. arently either of these conditions allows the toxic atom to ct with the metal catalyst.

It was found that the activity of a platinum catalyst poisoned h a compound such as diethyl sulfide could be restored by oxidizing sulfide to a sulfone in situ with hypochlorite.

. METALS AS POISONS

The toxicity of a number of metals (in the form of the aces) was determined with the same system and catalyst mentioned ve. Of the elements of the first four groups of the Bohr Table, e tested was toxic, with the exception of aluminum.

The toxic elements could be divided into three groups with ative toxicities of one, two and four. Toxicity increased with reasing atomic size and with the number of covalent bonds the ment might be expected to form with platinum.

References

Pease, J. Am. Chem. Soc. 45, 2296 (1923)
Maxted and Moon, J. Chem. Soc. 1938, 1228
Almquist and Black, J. Am. Chem. Soc. 48, 2814 (1926)
Yoshikawa, Bull, Inst. Phys. Chem. Research (Tokyo) 13, 1042, (1934) C.A. 29, 5005 (1935)
Maxted, J. Chem. Soc. 119, 225 (1921)
Maxted, J. Chem. Soc. 119, 1280 (1921)
Maxted and Morrish, J. Chem. Soc. 1940, 252
Maxted and Evans, ibid, 1937, 603
Maxted and Evans, ibid, 1937, 1004
Maxted and Evans, ibid, 1938, 455
Maxted and Marsden, ibid, 1938, 839
Maxted and Marsden, ibid, 1940, 469
Maxted and Morrish, ibid, 1941, 132

USES OF THE IONIC POTENTIAL

George K. Schweitzer March 18, 1947

I. The Ionic Potential (3)

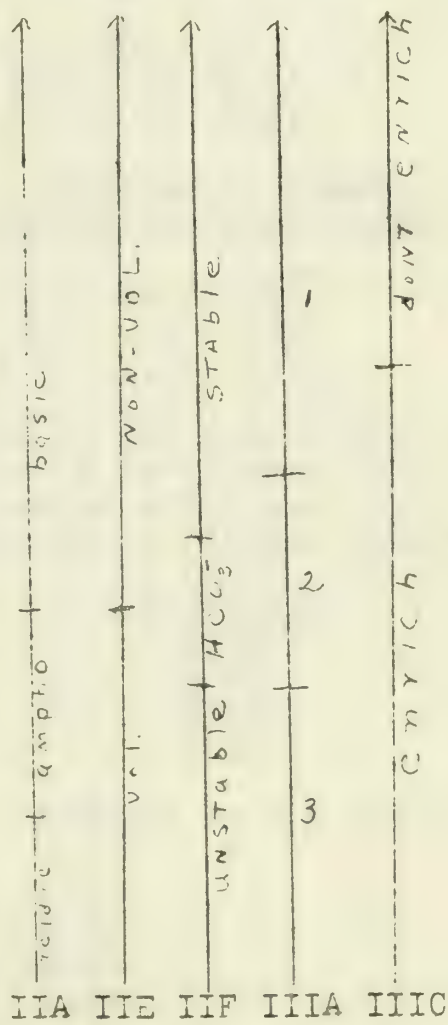
Quite frequently we are reminded that the ninety-six known chemical elements are too complex to be classified by reference to any one atomic characteristic. The periodic classification gives us only qualitative ideas and many attempts have been made to place the elements on a quantitative scale.

Two important factors influencing ionic behavior are ionic radius and oxidation number; increasing ionic radius and ionic charge acting in opposite directions. In view of these considerations, Cartledge has proposed that the ratio of charge to radius (of a cation) should be an important property. Hence he defines the ionic potential (ϕ) as:

$$\phi = \frac{Z}{} = \frac{\text{charge}}{\text{radius}}$$

Some actual values of the ionic potential are given in the following table:

Ion	Z	r	ϕ	$\sqrt{\phi}$
Cs	1	1.69	0.61	0.78
Rb	1	1.48	0.67	0.82
K	1	1.33	0.71	0.89
Na	1	0.98	1.00	1.00
Li	1	0.60	1.30	1.14
Ba	2	1.35	1.40	1.18
Sr	2	1.13	1.60	1.26
Ca	2	0.99	1.90	1.38
La	3	1.15	2.50	1.58
Mg	2	0.65	2.60	1.62
Sm	3	1.11	2.70	1.64
Y	3	0.93	2.80	1.67
Lu	3	1.00	3.00	1.74
Sc	3	0.81	3.60	1.90
Th	4	1.10	3.70	1.92
Ce	4	1.03	3.90	1.98
Zr	4	0.80	4.60	2.15
Al	3	0.50	5.30	2.30
Be	2	0.31	5.90	2.43
Ti	4	0.68	6.30	2.51
Cb	5	0.70	7.3	2.75
Mo	6	0.62	9.7	3.11
Si	4	0.41	10.0	3.16
B	3	0.20	15.0	3.88
P	5	0.34	15.0	3.88
S	6	0.29	20.0	4.46
C	4	0.15	27.0	5.20
N	5	0.11	45.0	6.70



II. Chemical Applications (3,4,5,7)

A. Acid and basic character may be related to ϕ as follows:

$\sqrt{\phi}$	Nature of hydroxide	example	$\sqrt{\phi}$
<2.2	basic	NaOH	1.00
>3.2	acidic	$P(OH)_5$	3.88
2.2-3.2	amphoteric	$Al(OH)_3$	2.30

B. The heats of solution (evolution) of salts with a common anion increase with the ϕ of the cation.

Cmpd.	Heat of Soln.	ϕ cation
LiCl	8.37kcal/mole	1.47
NaCl	-1.2	1.33
KCl	-4.4	0.75
RbCl	-4.5	0.68
CsCl	-4.75	0.60

C. The discharge potentials of cations in fused electrolytes decrease regularly with increasing ϕ.

Cation	Dischg. Pot.	ϕ cation
Al^{+++}	1.00 v.	6.0
Mg^{++}	1.45 v.	2.82
Ca^{++}	1.90 v.	2.04
Na^{+}	2.45 v.	1.02
Cs^{+}	2.95 v.	0.60

D. The ionization potentials of metals decrease with decreasing ϕ.

Element	Li	Na	K	Rb	Cs
Ioniz.	5.37	5.12	4.32	4.16	3.88
ϕ	1.30	1.00	0.71	0.67	0.61

E. If the $\sqrt{\phi}$ of the cation of a chloride is greater than 2.2, the chloride is volatile and non-conducting in the liquid state.

Element	Si^{+4}	Ge^{+4}	Ti^{+4}	Pb^{-4}	Th^{+4}
M.P. Cl^{-}	-70	-49.5	-30	-15	820
$\sqrt{\phi}$	3.16	2.74	2.51	2.18	1.92

F. Cations with $\sqrt{\phi}$ greater than 2 do not form stable normal carbonates or nitrates. When ϕ is between 2-2.5, basic carbonates may be precipitated in solution. They are then soluble in an excess of ammonium or alkali carbonate.

Cmpd.	Prop.	ϕ cation
$Sc_2(CO_3)_3$	stable	1.90
$Th(CO_3)_2$	stable	1.92
$Zr(CO_3)_2$	unstable	2.15
$Al_2(CO_3)_3$	unstable	2.30

G. Binary crystals increase in hardness as the ϕ's of their constituents increase.

Cmpt.	NaF	MgO	ScN	TiC
Hard.	3.2	6.5	7-8	8-9
$\sqrt{\phi m}$	1.00	1.62	1.90	2.51
$\sqrt{\phi a}$	0.86	1.19	1.32	1.24

H. When the ϕ of a cation is less than 1, its salts are seldom hydrated and it does not form complex compounds. If the ϕ lies above 1.9, the salts are almost invariably hydrated. Ions with a ϕ above 2.4 are readily ammoniated and those with ϕ above 2.5 may form ammines and inner complexes. The following table lists some of the common complexing ions and shows how these rules work.

Ion	ϕ	Complexing Ability
Cs^{+}	0.61	
Rb^{+}	0.67	1
K^{+}	0.71	
Na^{+}	1.00	
Be^{++}	1.4	
Hg^{++}	1.8	
Cd^{++}	1.9	
Ca^{++}	1.9	
Zn^{++}	2.4	
Co^{++}	2.4	
Ni^{++}	2.5	
Fe^{+++}	4.5	2
Co^{+++}	4.5	3
Cr^{+++}	4.6	4
Al^{+++}	6.0	
Pt^{++++}	6.0	

II. Geological Applications (1,2,6)

A. Elements may be divided into three groups geologically:

1. Cations with ϕ less than three-these cations remain in true ionic solution during the processes of weathering and transportation.
2. Cations with ϕ between 3 and 6-these cations are precipitated by hydrolysis.
3. Cations with ϕ greater than 6-these cations form complex anions containing oxygen and some of them are soluble.

B. Natural zeolites collect and easily exchange cations whose ϕ's are less than 2.

C. Elements with high values of ϕ enrich in silicates; Goldschmidt says that the dividing line is at ϕ equal to 2.6.

. Conclusion

From the above data we see that the ionic potential is a convenient aid for instruction and understanding of various phenomena. The user is warned, though, because the concept is not infallible and may fail in some cases. It is used to greatest advantage in trend predictions; but at times other factors may make it invalid, chief among these being the effect of the covalent bond.

References

1. Goldschmidt, J. Chem. Soc. 1937, 655.
2. Goldschmidt, Geochemische Verteilungsgesetze der Elemente IX. Die Mengenverhaltnisse der Element und der Atom-Arten. Skr. Norske Vid-Akad. Oslo, Mat. Natwiv. Kl., No. 4, 1937.
3. Cartledge, J. Am. Chem. Soc. 50, 2855 (1928).
4. Cartledge, J. Am. Chem. Soc. 52, 3076 (1930).
5. Sun, J. Chinese Chem. Soc. 5, 148 (1937).
6. Rankama, Suomen Geol. Toimikunta, Bull. Comm. geol. Finlande, 126, 24 (1941)
7. Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry", p. 166.

TETRAVALENT NICKEL

Elliot N. Marvel ROLL CALL March 25, 1947

Tetravalent nickel is not very stable or well characterized. The oxide NiO_2 does exist perhaps, but has never been obtained pure and with constant composition. Hall (1) has obtained some heteropolyacids of molybdenum and nickel with Ni^{+4}. Reasonably complete analytical data and oxidative studies substantiate this claim. His salts have the formula $3MO \cdot NiO_2 \cdot 9MoO_3 \cdot xH_2O$ where M may be K_2, $(NH_4)_2$, or Ba. All are purple-black insoluble solids which give very dilute but deep purple solutions.

Ray and Sarma (2) have submitted Hall's complexes to magnetic studies. All are diamagnetic showing that the Ni^{+4} is the central atom of an octahedral complex with d^2sp^3 hybrid bonds resembling Co^3. These authors have also prepared some tetravalent nickel complexes as $M(I)[NiIO_6]$. Both Hall and Ray and Sarma found that the only effective oxidizing agent was an alkalie persulfate. The treatment of a boiling $NiSO_4$ and M_5IO_6 solution with alkalie persulfate precipitates the insoluble purple-black complexes as microcrystalline solids. Analytical data are not presented but would not serve to distinguish the Ni^{+4} from Ni^{+2}. Tetravalent nickel having four unpaired electrons should have a magnetic susceptibility of 4.9 Bohr magnetons. The complexes however have a susceptibility of only 1.2 magnetons. Dissociation of the diamagnetic complex as shown would account for this abnormality.

$$M[NiIO_6] \rightleftharpoons MIO_4 + NiO_2$$

However until fully quantitative oxidation studies can confirm the presence of Ni^{+4} this series falls in the same category as the higher oxides of nickel.

References

1. Hall, J. Am. Chem. Soc. 29, 692 (1907)
2. Ray and Sarma, Nature, 157, 627 (1946)

THE BUILDERS* by Vannevar Bush

Leon S. Ciereszko ROLL CALL March 25, 1947

The process by which the boundaries of knowledge are advanced, and the structure of organized science is built, is a complex process indeed. It corresponds fairly well with the exploitation of a difficult quarry for its building materials and the fitting of these into an edifice; but there are very significant differences. First, the material itself is exceedingly varied, hidden and overlaid with relatively worthless rubble and the process of uncovering new facts and relationships has some of the attributes of prospecting and exploration rather than of mining or quarrying. Second, the whole effort is highly unorganized. There are no direct orders from architect or quarrymaster. Individuals and small bands proceed about their businesses unimpeded and uncontrolled, digging where they will, working over their material, and tucking it into place in the edifice.

Finally, the edifice itself has a remarkable property, for its form is predestined by the laws of logic and the nature of human reasoning. It is almost as though it had once existed, and its building blocks had then been scattered, hidden, and buried, each with its unique form retained so that it would fit only in its own peculiar position, and with the concomitant limitation that the blocks cannot be found or recognized until the building of the structure has progressed to the point where their position and form reveals itself to the discerning eye of the talented worker in the quarry. Parts of the edifice are being used while construction proceeds, by reason of the applications of science, but other parts are merely admired for their beauty and symmetry, and their possible utility is not in question.

In these circumstances it is not at all strange that the workers sometimes proceed in erratic ways. There are those who are quite content, given a few tools, to dig away unearthing odd blocks, piling them up in the view of fellow workers, and apparently not caring whether they fit anywhere or not. Unfortunately there are also those who watch carefully until some industrious group digs out a particularly ornamental block, whereupon they fit it in place with much gusto and bow to the crowd. Some groups do not dig at all, but spend all their time arguing as to the exact arrangement of a cornice or an abutment. Some spend all their days trying to pull down a block or two that a rival has put in place. Some, indeed neither dig nor argure, but go along with the crowd, scratch here and there, and enjoy the scenery. Some sit by and give advice, and some just sit.

On the other hand there are those men of rare vision, who can grasp well in advance just the block that is needed for rapid advance on a section of the edifice to be possible, who can tell by some subtle sense where it will be found, and who have an uncanny skill in cleaning away dross and bringing it surely into the light. These are the master workmen. For each of them there can well be many of lesser stature who chip and delve, industriously, but with little grasp of what it is all about, and who nevertheless make the great steps possible.

There are those who can give the structure meaning, who can trace its evolution from early times, and describe the glories that are to be, in ways that inspire those who work and those who enjoy. They bring the inspiration that all is not mere building of monotonous walls, and that there is architecture even though the architect is not seen to guide and order.

There are those who labor to make the utility of the structure real, to cause it to give shelter to the multitude, that they may be better protected, and that they may derive health and well-being because of its presence.

And the edifice is not built by the quarrymen and the masons alone, There are those who bring them food during their labors, and cooling drink when the days are warm, who sing to them, and place flowers on the little walls that have grown with the years.

There are also the old men, whose days of vigorous building are done, whose eyes are too dim to see the details of the arch or the needed form of its keystone; but who have built a wall here and there, and lived long in the edifice, who have learned to love it and who have even grasped a suggestion of its ultimate meaning; and who sit in the shade and encourage the young men.

SEPARATION OF RADIOISOTOPES

O. F. Hill ROLL CALL March 25, 1947

Radiochemistry involves the handling of extremely small amounts of material (for example, one microcurie of an element of atomic weight 100 and of half life 1 day consists of only 7.7×10^{-13} gm.) so that the normal techniques of chemical separations do not apply. This material, however, has the same chemical properties as the stable isotopes of that element and those properties are brought into use in its separation. A qualitative outline is presented of the different methods of separation employed.

I. Separation by means of Carriers.

Frequently it is advantageous to separate a radioelement by "diluting" the radioisotope with a stable isotope. The stable isotope is called a carrier. Carriers are used, for example, when it is desired to determine which of several possible nuclear reactions may have occurred in a particular bombardment. Accordingly, in the nuclear reaction.

$$Z^a + n \longrightarrow \begin{cases} Z^{a+1} + \gamma \\ (Z-1)^a + p \\ (Z-2)^{a-3} + \alpha \end{cases}$$

About 10 mg of each new element which might be formed (e.g., Z-1 and Z-2) are added and the usual chemical separations carried out, the radioactive product thus following its isotope in the separation.

II. Separations without carriers

A. Precipitation Reactions

After the bombardment, $Cu^{65}(d,2n)Zn^{65}$, the target may be dissolved and the copper precipitated as the sulfide, leaving the zinc in solution. Similarily, "scavengers" can be employed. Precipitates such as MnO_2 or $BaSO_4$, which pick up substances present even in macro amounts, may be utilized to remove certain of the fission products from solution, leaving others in solution.

B. Electroplating and chemical plating

After the bombardment, $Zn^{64}(n,p)Cu^{64}$, the target may be dissolved and the copper plated out on lead.

C. Volatility Methods

After the bombardment, $Ga^{71}(D,2n)Ge^{71}$, $GeCl_4$ may be volatilized from hydrochloric acid solution without carrier other than vapors from the solution.

Element 85 has been separated from bismuth after the bombardment $Bi^{209}(\alpha,2n)85^{211}$ by heating the target to 400°C, at which temperature element 85 readily volatilzes and which is, well below the boiling point of Bi(1470°C).

Hahn and Strassmann passed a current of air thru solutions of uranium compounds to remove krypton and zenon activities from among the fission products.

D. Non Aqueous Extractions

After the bombardment $Zn^{67}(d,n)Ga^{68}$, a6N hydrochloric acid solution of the target may be shaken with ether, extracting 99.5% of the gallium into the ether layer, just as with macro amounts.

E. Adsorption

Adsorption is a source of trouble more than an aid. For example, in the determination of the solubility of $RaSO_4$, low values were obtained because > 98% of the $RaSO_4$ from its saturated solution was adsorbed on filter paper. Glassware picks up large amounts of radioactive materials and is a frequent source of contamination.

F. Leaching

After the bombardment, $Mg^{24}(d, \alpha)Na^{22}$, the sodium may be leached from a magnesium oxide target.

III. Separation by Recoil-The Szilard-Chalmers Method

When the radioelement formed is on isotope of the target, a special technique is employed to increase the concentration of the radioisotope in the element. For example, in the reaction, $Br^{79}(n, \gamma)Br^{80}$, the γ recoil causes disruption of molecules such as C_2H_5Br and C_6H_5Br and the active bromine can be collected (usually with bromine carrier) free from the organic molecule. Similarily, upon bombardment of BrO_3^-, the active bromine can be collected as silver bromide.

Necessary conditions are

(1) The radio atoms must be liberated during the bombardment reaction.

(2) The radio atoms must not exchange with the unchanged atoms.

(3) The radio atoms must be separable from the remaining atoms.

IV. The Hahn precipitation rules

Frequently, it is necessary to employ as carrier on element which is not an isotope of the radioelement which is to be separated (e.g., the separation of $RaSO_4$ with $BaSO_4$). In 1913 Fajans formulated the rule that the lower the solubility of the compound formed by the radioelement with the anion of the precipitate, the greater the amount carried by the precipitate. For example, RaC (Bi isotope) precipitates with $BaCO_3$ and with $Fe(OH)_3$ but not with $BaSO_4$ or $PbSO_4$, in agreement with the known solubility of the bismuth salts.

Hahn has divided coprecipitation into four types of processes:

(1) Isomorphous replacement is the precipitation process when true isomorphism of the components occurs. The amount of carrying is independent of temperature, acidity, order of addition reagents, etc., as would be expected.

(2) Surface adsorption is the coprecipitation of an element on the active surface of a freshly formed precipitate. It is favored when the precipitate forms with a surface charge opposite to that of the ion to be carried. Such things as temperature, acidity, order of the addition of the reagents, etc. greatly influence the efficienty of this method.

(3) Anomalous isomorphous replacement is similar to (1) except that it is not observed in macroscopic amounts of the two components. It has been suggested that a very narrow range of solid solution of the compound of the radioelement in the compound of the carrier element may be formed.

(4) Internal adsorption systems are poorly understood. The crystals appear as if the mother liquor or a radio-colloid is mechanically enclosed within the crystal. X-rays indicate spotty distribution of the tracer element.

Source of Material: Series of lectures presented by G.T.Seaborg at the Metallurgical Laboratory, University of Chicago, July, 1942.

A few general references:

Hahn, Applied Radiochemistry, 1936-Hevesy&Paneth, Manual of Radioactivity, 2nd ed., 1938.-Seaborg, Artificial Radioactivity, Chem Rev. 27 199-285 (1940)

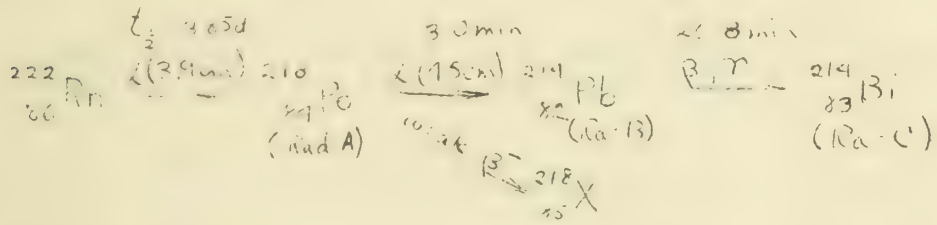
ELEMENTS 85 AND 87

Caryle Shoemaker April 1, 1947

The gaps in the periodic table have been filled one by one until at the present time there seems to be few undiscovered elements. The unknown as well as many of the rare elements are found in the lower part of the periodic table. Many of the elements with high atomic numbers, especially those whose number is greater than 83 have radioactive isotopes. Because of this and the fact that elements 85 and 87 are very rare if they exist naturally at all, it was widely suspected that these elements would be radioactive with comparatively short half lives.

Hulubei and Cauchois (1) in 1939 were among the first to report some experiments which they interpreted as evidence for the existence of 85 in the decay products of radon.

Minder (2) also proposed that element 85 was among the products of radium A (Po) by a branched reaction.



Their conclusions for evidence of 85 are based on the ionization of shielded gas chambers (to stop α particles). It was found in this connection that Rn would coagulate starch.

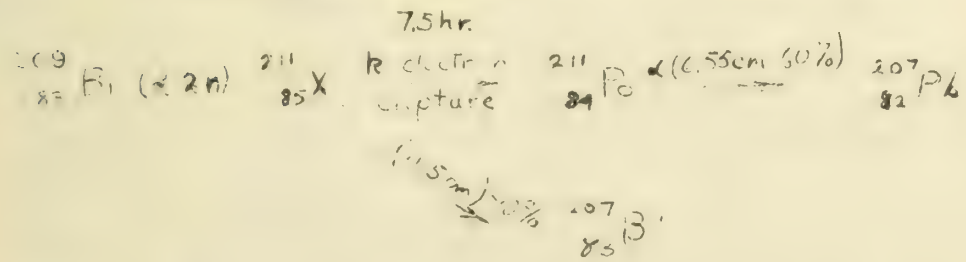
The first to actually report the properties of element 85 were Carson, MacKenzie and Segre who bombarded Bi with 32 mev. alpha particles at the University of California in 1940. As a result of the bombardment the following radioactive phenomena were observed.

1. Alpha particles of 6.55 cm. range (60% of the total).
2. Alpha particles of 4.52 cm. range (40% of the total).
3. Gamma rays with an energy of about 0.5 m.e.v.
4. An X-ray or soft gamma ray with an energy of about 80 k.e.v.
5. A soft X-ray.
6. A few low energy electrons.
7. All exhibit a half life of 7.5 hours.

Further evidence and the basis for their conclusions on the nuclear processes are as follows.

1. Alpha tracks always appear singly.
2. Nuclear isomerism was ruled out because the Geiger Nuttal rule would predict a half life of 10^{-3} seconds instead of the obseroed 7.5 hours. It would be most reasonable to assume that the 4.5 c m appeared first.

3. A right angled tube was arranged so that the nuclei recoiling from one alpha disintegration would be collected in front of a counter. The alpha particle from a second disintegration would be detected. None were found. This would indicate that a branching reaction has occurred.
4. The fact that both alpha particles have the same half life suggest that both groups originate from the same species through some intermediate process.
5. The X-rays were characteristic of Po and had a half life of 7.5 hours.
6. No positrons were found. The nuclear reactions were concluded to be,



Though element 85 was separated from Bi in ten sec., no evidence was found for the reaction

$$^{207}_{83}Bi \xrightarrow{k\text{-electron capt.}} {}^{207}_{82}Pb$$

Fission was ruled out because of the simplicity of the radioactive phenomena and elements of lower number occuring as a result of fission would probably not be alpha emitters.

The reactions of element 85 were studied by the tracer method using carriers and are reported as follows:

1. If the target of bismuth was scraped and the filings heated almost to the melting point in an inert atmosphere, the active residue was found to collect in an invisible layer on a cooled plate. The target was dissolved in nitric acid and diluted to 0.25 N (H^+) for the following reactions.
2. HCl does not precipitate 85 using Pb or Tl as a carrier (useful for separating Hg, Pb, Tl)
3. 85 does not ppt. quantitatively from $(NH_4)_2S$ solution using Ag or Hg as a carrier. Hydrogen sulfide will precipitate 85 quantitatively in acid solution up to 6N HCl using Bi, Hg, Ag, Sb.
4. Ammonium hydroxide or fixed alkali precipitates 85, perhaps due to absorption (not quantitative).
5. Fractional hydrolysis of bismuth nitrate by dilution enriches 85 in the first fractions.
6. Reducing agents such as sulfur dioxide, zinc or stannous chloride in hydrochloric or sulfuric acid solution precipitate 85 quantitatively. Precipitation with sulfur dioxide in 3N HCl offers a means of separating 85 quantitatively from polonium which stays in solution. Sodium stannite does not precipitate 85 and this reaction affords a good method for separating it from bismuth, tellurium, selenium, mercury, etc.

7. Silver nitrate does not precipitate 85 from a slightly acid solution using iodide as a carrier. When AgI, Zn and sulfuric acid are mixed the activity collects on the zinc.

Compound	Solubility
$AgCl$	8.9×10^{-5} $\frac{gms}{100\ ml}$
$AgClO_3$	10
$AgClO_4$	525 (deliquescent)
$AgBr$	8.9×10^{-6}
$AgBrO_3$	0.81
AgI	3×10^{-7}
$AgIO_3$	0.003

8. KI and dilute nitric acid were heated and the liberated iodine distilled. The recovery of iodine was practically complete while the recovery of 85 was variable and poor. Polonium does not distill.

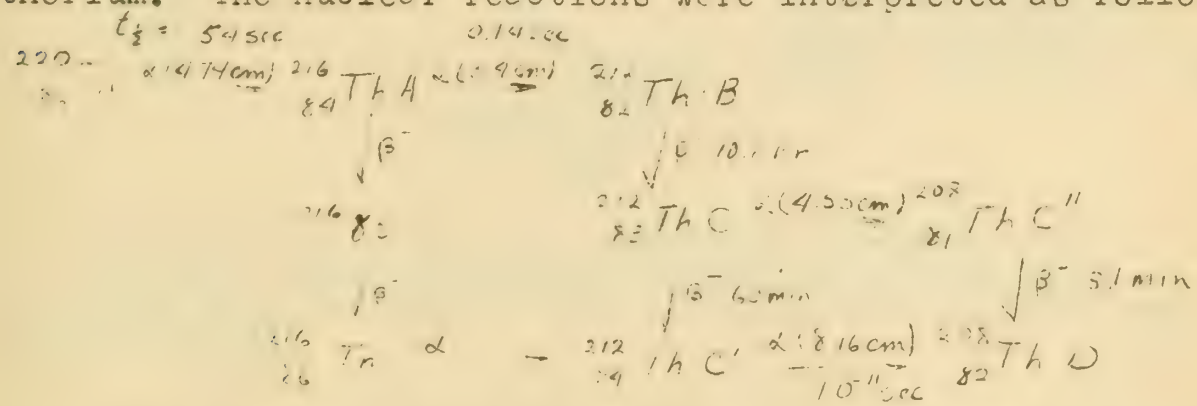
9. Extraction of 85 and iodine with carbon tetrachloride gave a poor but definite yield.

10. 85 is deposited on a copper plate from a 0.25 N nitric acid solution containing bismuth and mercury. Cautious heating removed the mercury leaving 85 behind.

Hamilton and Mayo (4) used some of the element 85 as prepared by Carson, MacKenzie, and Segre to inject into guinea pigs. It was found that 85 was concentrated up to 100 times in the thyroid gland.

Recently Carson, MacKenzie and Segre proposed the name astatine (At) meaning unstable, for element 85. (5,6).

Leigh, Smith, and Minder (7) (1942) have reported that they detected an isotope of 85 in the decay products of radiothorium. The nuclear reactions were interpreted as follows.

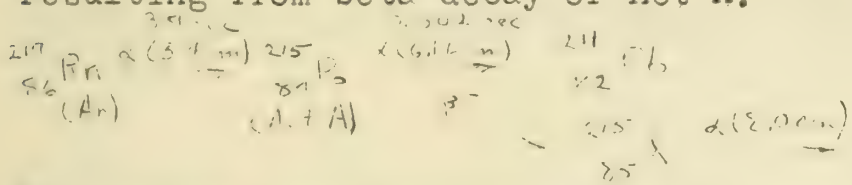


The element 85 was separated from Rd-Th by blowing the Th between two copper electrodes. 85 was collected on the negative electrode and sublimed at 180° onto a cooled silver wire. After 10 min. the wire was placed in a Wilson expansion chamber. Alpha and beta tracks began to appear after 10-20 min. These tracks originated from the gas and the walls, continuing for about 2 days. A beta ray often started at the same point as an alpha particle. No reactions were given.

In 1942 (8) Karlik and Bernest at the Vienna Institute for Radium Research disputed the earlier results Hulubei, Cauchois and Minden. They could find no evidence of weak beta radiation from radium A.

Later in (1943) they continued the work of Leigh, Smith and Minden and concentrated the emanation from Rd-Th. Alpha radiation of 6.84 cm. range and half period 54 sec. was found. They believe this to be due to an alpha radiating isotope 216 of element 85. The branching ratio compared with the alpha disintegration of Th A was determined as 1.35×10^{-4}. They could not duplicate the work of Leigh, Smith and Minden concerning the separation of element 85.

In a third paper they claim to have found 85 in the products of An. Alpha rays reaching beyond the longest radiation of the active precipitate (6.6 cm) were observed in an ionization chamber with 4-step electrometer and oscillograph. An alpha radiation of range 8.0 cm. in the ratio 5×10^{-6} to the Act A radiation was found. This value corresponds to an extrapolsted energy for element 85 of mass 215 resulting from beta decay of Act A.



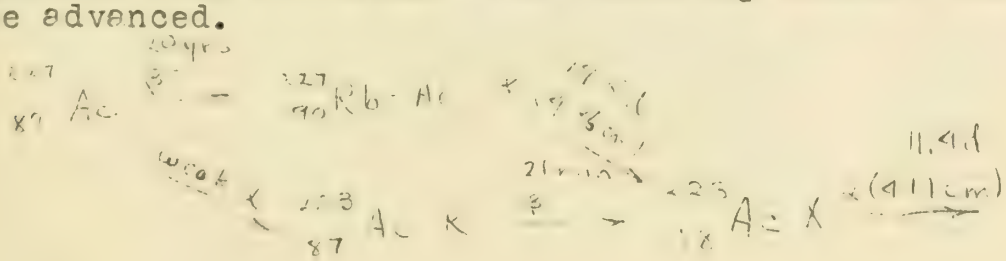
No chemical reactions were given.

The following isotopes of 85 have been reported.

Isotope	Radiation	Experimenter
218	(?)	Hulubei, Cauchlis, Minder
216	β^-	Leigh, Smith, Minder
216	α	Karlik and Bernert
215	(?)	Karlik and Bernert
211	α (4.5 cm. 40%) kelectron capt. 60%	Corson, MacKenzie, Segre

Much less is known, (or reported) on Element 87

In 1939, Perey (9) found evidence of a weak alpha radiation from actimium. The following nuclear reactions were advanced.



This new element was not carried down by precipitates of lead sulfide, barium carbonate or ceric hydroxide. It was found to react, with cesium as a carrier, to form an insoluble perchlorate. Recently the name francium (Fr) was proposed for this element (5,6).

BIBLIOGRAPHY

1. Hulubei, H., and Cauchois, Y., Comptes rendu. 209, 39 (1939).
2. Minder, W., Helv. Phys. Acta. 13, 144-152 (1940)
3. Corson, D. R., MacKenzie, K. R., and Segre, E. Phys. Rev. 57, 459, 1087, 58, 672 (1940).
4. Hamilton, J. G. and Sole y, M. H., Proc. Natl. Acad. Sci. U. S. 26, 483-9 (1940).
5. Paneth, . F. A. Nature, Jan. 4, 1947.
6. Chem. and Engr. News. 25, 431 (1947).
7. Leigh-Smith, A. and Minder, W., Nature 150, 767-8 (1942).
8. Karlik, Berta and Bernert, Traude Naturwissenschaften 30, 685-6 (1942); 31, 492 (1943); 32, 44 (1944).
9. Perey, M. J. Phys. et le Radium 10, 435, 438 (1939).
10. Perey, M. Compt. rend. 208, 97 (1939); 212, 893 (1991).
11. Perey, M. and Lecoin, M., Nature 144, 326 (1939)

METHODS OF DETERMING THE ADSORPTION OF GASES AND VAPORS ON SOLIDS

W. G. Britton April 8, 1947

I. Introduction

Volumes have been written on the topic of adsorption. This discussion is confined to the methods used to measure the adsorption of vapors by solids with only a brief discussion of the theory involved.

II. Theory

A. Variables to consider

If we consider, for example, the adsorption of vapors by charcoal, the pressure of the vapor, according to the phase rule, should be determined by the type of charcoal, the type of vapor, the concentration of the condensed phase and the temperature. Coolidge (1) has shown additional variables which are listed below.

1. The temperature of the charcoal during outgassing
2. The time for outgassing.
3. The efficiency of the outgassing pump.
4. The previous exposure of the charcoal to the same or other vapors.
5. The direction from which equilibrium is approached.
6. The time elapsed since the last change in concentration.

This last variable is unusual. An equilibrium between the charcoal and gas phase is quickly reached, after which the pressure decreases in a few hours because the vapor slowly penetrates to the interior of the charcoal. Sometimes the pressure increases again, probably because traces of gas which remain in the charcoal after outgassing are replaced by the penetration of more powerfully adsorbed vapors.

B. Adsorption Isotherms

When the amount of gas adsorbed is plotted against pressure, an "S" shaped curve usually results. Allmand and Burrage (2) have shown that if a sufficient number of points are obtained, some adsorption isotherms show discontinuities. These breaks escaped the notice of other investigators because an insufficient number of points was obtained experimentally, and the deviation of a particular point from the smooth curve was attributed to experimental error.

C. Character of the Interaction

When a gas comes in contact with a solid, it may be adsorbed on the surface of the solid, it may be absorbed by diffusion into the solid or it may react with the solid. Benton (3) has shown that absorption may be distinguished from adsorption by study of the plot of pressure of the gas against time. Since gases diffuse into or through solids slowly, the pressure decreases rapidly till adsorption equilibrium is reached, then slowly till absorption equilibrium is reached. A chemical reaction may be distinguished only by a knowledge of the tendency of a particular gas to react with a particular solid. Generally, a gas will act in all three manners simultaneously.

D. Mathematical Treatment

Even though the process of adsorption is a complicated one, several mathematical equations have been proposed.

Freundlich has proposed a simple equation which is faulty because it does not recognize a maximum saturation for a definite area of adsorbing surface (4).

Langmuir has proposed an equation which assumes that an adsorption maximum or surface saturation may be obtained (4). Langmuir described the mechanism of adsorption as a dynamic equilibrium between condensation and evaporation. When the surface becomes covered with an unimolecular thickness of adsorbed gas, the surface is saturated.

Brunauer, Emmett, and Teller (5) have modified the Langmuir concept. They suggested that a multi-molecular layer may be built up, and they derived two equations patterned after the Langmuir equation for a mono-molecular layer. Pickett changed the equations (6) by modifying the assumption that the final layer of vapor on an element of surface is fully exposed regardless of the number of layers on any adjacent element of surface. He has suggested a decrease in the probability of escape from an elemental area covered with a number of layers when the number of layers on adjacent areas increases, and has derived an equation which is verified over a greater range than the Brunauer, Emmett, and Teller equations.

Recent investigators have applied mathematical treatment to the discontinuities in the isotherms (7). Most changes in phase are of the first order, i.e. posess a latent heat of transformation and a discontinuous change in volume. In a first order change the volume changes without a corresponding change in pressure; in a second order change there is a discontinuity in $(\partial V/\partial P)_T$ and in a third order change there is a discontinuity in $(\partial^2 V/\partial P^2)_T$. The order of the change of phase accounts for various types of discontinuities in experimental data. Such a complex problem as this entails careful work in experimental verification.

III. Methods

There are three general methods for measuring adsorption. The static method involves passing a known quantity of vapor into a vessel containing the adsorbent and comparing the observed pressure with that which would have existed had there been no adsorption. The dynamic method involves saturating the solid with the adsorbent, passing another gas over the saturated solid at a given rate and measuring the decrease in weight of the solid at intervals. The sorption balance method depends on the gain in weight of the solid as determined by the lengthening of a spring to which it is attached. Other methods involving the change in the floating level of a hydrometer, the use of an ultra-violet photometer, and the determination of adsorption of mixed gases will be presented.

A. The Static Method

A simple and rapid technique has been described by Porter (8). The solid was placed on a micro-filter tube and the filter tube was placed inside a larger tube which was connected to a vacuum line and evacuated. Vapor was introduced into the tube and the region around the solid was cooled so that the vapor condensed on the solid. The filter was removed and the excess liquid was centrifuged off. The filter was weighed to determine the weight of the solid saturated with vapor. The filter was returned to the tube; the tube was evacuated to a desirable pressure, and the filter was removed and reweighed. From the

data obtained, the pressure was plotted against the volume adsorbed.

Work on the adsorption of sulfur dioxide has been described by McGavack and Patrick (9). The quantity of gas introduced onto a weighed quantity of solid was determined with a gas buret and the quantity of gas withdrawn was determined by the gain in weight of a tube of soda lime into which some of the gas was allowed to escape.

A complicated apparatus for static measurements has been described by Coolidge (1). All valves were mercury seals. Pressures were measured with a McCleod gauge and a quartz fiber gauge and volumes were measured with calibrated measuring bulbs. During a run, the quantity of gas in the apparatus was never altered, but the fraction adsorbed by the solid was obtained from the pressure readings. The weight of the solid was obtained by sealing off the evacuated tube, weighing, and subtracting the weight of the glass.

B. The Dynamic Method

The dynamic method of Allmund and Burrage (10) consisted of passing air saturated with vapor over the solid, weighting it, then passing dry air at a known rate over the solid (as determined by a flow meter) and removing it at various intervals and weighing. The weight of the adsorbed vapor was plotted against the volume of air passed. The tangent to this curve represents the rate of loss of sorbed vapor and is proportional to the pressure of the vapor.

In a more recent article, Burrage has shown a source of error in their earlier determination (11). When the air passed through the tube of solid, the adsorbed vapor at the lower end of the tube passed into the air first so that there was a gradient set up within the tube. A modified tube which had a volume of less than one centimeter was then used because here (Burrage calculated) the pressure length effect was insignificant. The data obtained from both of these investigations showed discontinuities in the isotherms. Some of the criticisms of this method and the replies Burrage gave are interesting.

Criticism: It is unlikely that equilibrium was reached between the adsorbed vapor and the air stream.
Reply: It was shown that the results were independent of the velocity of the air stream.
Criticism: True equilibrium was not attained. If more time were allowed the adsorbed material would "sink in".
Reply: The vapor was allowed to stand over the solid for twenty-four hours without a preciptible change in the pressure so "sinking in" did not occur with the materials used.
Criticism: Breaks in the isotherms might be connected with interruptions due to the necessity of weighing.
Reply: A determination was carried out with purposely long and short periods between weighings and breaks occurred at the same pressures as before.

Bohart and Adams (12) used a dynamic method for determing the effect of moist air on the adsorption of chlorine by charcoal. Air was passed through a flow meter, then through sulfuric acid of known concentration to give it a definite vapor pressure. Chlorine was passed through a flow meter, then mixed with the air. The mixture was passed through the chaircoal, then through a solution of potassium iodide and starch. The appearance of

chlorine beyond the charcoal was detected by the starch coloration. Titration of the potassium iodide solution with thiosulfate gave the amount of chlorine that the charcoal did not retain. The hydrogen chloride that was formed by catalytic action of the charcoal was determined by titrating the potassium iodide solution with sodium hydroxide.

C. The Sorption Balance Method

McBain and Baker (12) have described a sorption balance. The solid was placed on a pan attached to a spring which was sealed along with a small tube of volatile liquid into a larger bulb which was then evacuated. The tube of liquid was broken and the weight of vapor adsorbed was proportional to the elongation of the spring. The pressure of the vapor was regulated by regulating the temperature of the liquid.

Application of the sorption balance to high pressure measurements has been described by McBain and Britton (13). The balance was made of glass covered with a sheet iron screen. The balance was connected by copper tubing to a cylinder of compressed nitrogen. Thirty atmospheres pressure was handled by the apparatus. When it was desired to reduce the pressure a valve was loosened to permit some of the nitrogen to escape. The pressure was measured by a pressure gauge.

D. Miscellaneous Methods

A new technique has been described by Chambers and King (14). Their apparatus was essentially a modified sorption balance. A hydrometer floating in mercury held the solid and the change in weight of the solid was determined by the change in the level of the hydrometer.

Hurst and Rideal (15) have described a method for determining the selective adsorption of mixed gases. The composition of the gas was determined by measuring each pure gas in a gas buret, then mixing. The gas was then passed over the solid and the change in composition detected by thermal conductivity measurements.

Recent work on an automatic recording ultra-violet photometer has been described by Klotz and Dole (16). This device measured the rate of adsorption of a gas. The device works for any gas that adsorbs ultra-violet light. A concentration of one part per million has been detected.

REFERENCES

1. Coolidge, A. S., J. Am. Chem. Soc. 46, 596 (1924).
2. Allmund, A. J. and Burrage, L. J., Proc. Roy. Soc. (London) A130, 610 (1931).
3. Benton, A. F., J. Am. Chem. Soc. 45, 887 (1923).
4. Rideal, "Surface Chemistry", Cambridge University Press, Cambridge, England, 1926, p. 132.
5. Brunauer, S., Emmett, P., and Teller, E., J. Am. Chem. Soc. 60, 309 (1938).
6. Pickett, G., J. Am. Chem. Soc. 67, 1958 (1945).
7. Jura, G. et al., J. Chem. Phys. 14, 117 (1946).
8. Porter, J. L., J. Phys. Chem. 37, 361 (1933).
9. McGavack, J. Jr. and Patrick, W. A., J. Am. Chem. Soc. 42, 946 (1920).
10. Allmund, A. J. and Burrage, L. J., J. Soc. Chem. Ind. 47, 372T (1928).
11. Burrage, L. J., J. Phys. Chem. 34, 2202 (1930).
12. McBain, J. W. and Baker, A. M., J. Am. Chem. Soc. 48, 690 (1926).
13. McBain, J. W. and Britton, J. T., J. Am. Chem. Soc. 52, 2198 (1930).
14. Chambers, H. H. and King, A., J. Chem. Soc. 139 (1939).
15. Hurst, W. W. and Dideal, E. K., J. Chem. Soc. 125, 696 (1924).
16. Koltz, I. M. and Dole, M., Ind. Eng. Chem. (Anal. Ed.) 18, 741 (1946).

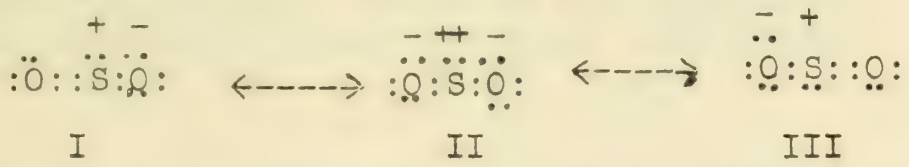
GENERAL REFERENCE

Deitz, V. R., "Bibliography of Solid Adsorbants" Washington, D.C., 1944.

ADDITION COMPOUNDS OF SULFUR DIOXIDE

Carl Weatherbee April 15, 1947

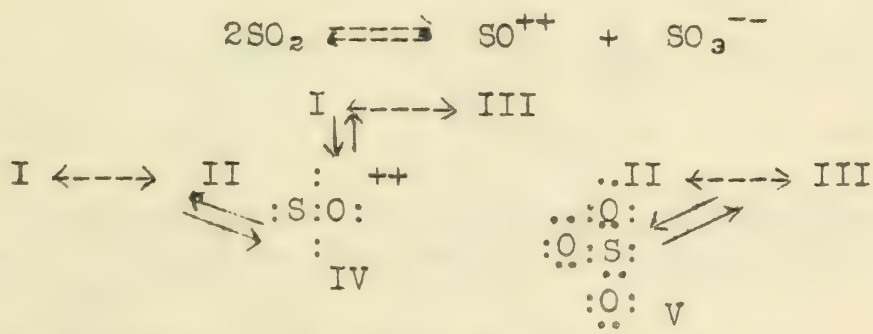
Sulfur dioxide is generally assumed to exist in the following resonance forms: (11)



I II III

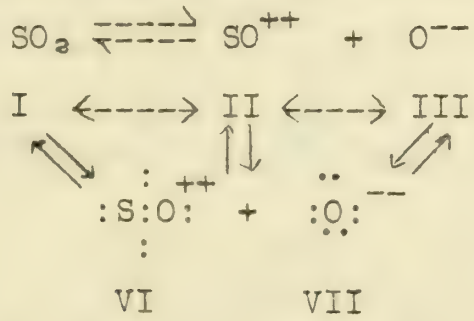
If the above is accepted as the structure of sulfur dioxide, then one can readily see that it is theoretically possible for both the sulfur atom and the oxygen atoms to act as electron donors and for the sulfur atom to act as an acceptor. The sulfur atom of II having only six electrons in its outer shell should be able to react by accepting a pair of electrons, whereas the sulfur atom and the oxygen atoms of either I, II, or III should be able to serve as electron pair donors. Moreover, evidence will be presented later indicating an oxygen atom can act as an acceptor.

Liquid sulfur dioxide is a fair solvent for many inorganic compounds and an excellent solvent for many organic substances; such solutions are good electrical conductors, while sulfur dioxide is not. It may be that liquid sulfur dioxide dissociates:



IV V

or it may dissociate as Wickert (8) has pointed out:

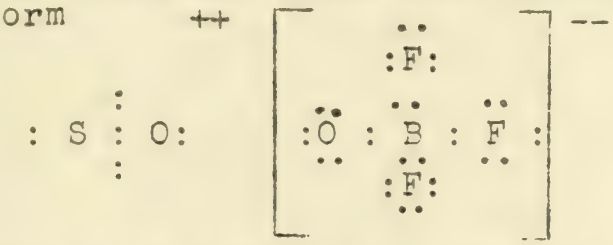


VI VII

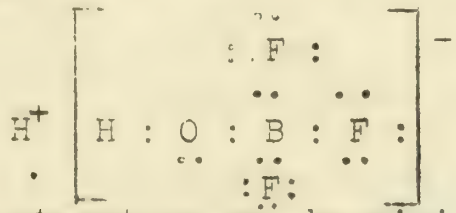
Even if sulfur dioxide should dissociate to any appreciable extent according to either of these mechanisms, there are good possibilities of the sulfur atom acting as an acceptor and the oxygen and sulfur atoms acting as donors.

Booth and Martin (13) have shown that boron trifluoride and sulfur dioxide form a 1:1 addition compound with sulfur dioxide. This was indicated by plotting temperature against mole fraction of boron trifluoride and obtaining a maximum at 50 mole percent of boron trifluoride.

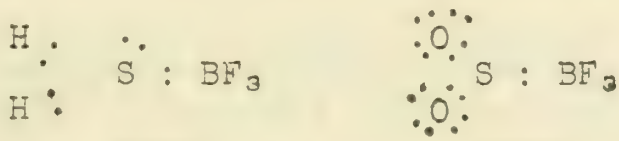
The question arises - what is the structure of this compound? If Wickert's theory of the dissociation of liquid sulfur dioxide is true, the boron trifluoride may react with VI and VII to form



in which the boron atom acts as an acceptor and the oxygen anion acts as a donor. This structure is analogous to that of the monohydrate of boron trifluoride:

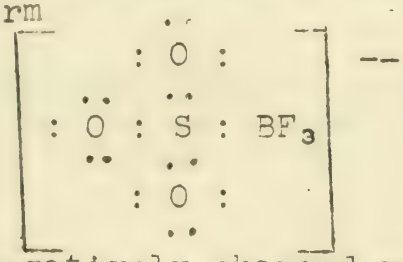


However, the structure may be similar to that of the addition compound between hydrogen sulfide and boron trifluoride VIIIa in which the sulfur atom acts as a donor:

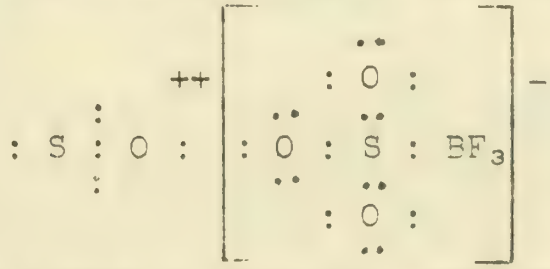


VIIIa VIIIb

Moreover, although it is not mentioned in literature, it seems that it should be theoretically possible for the sulfite anion V to form

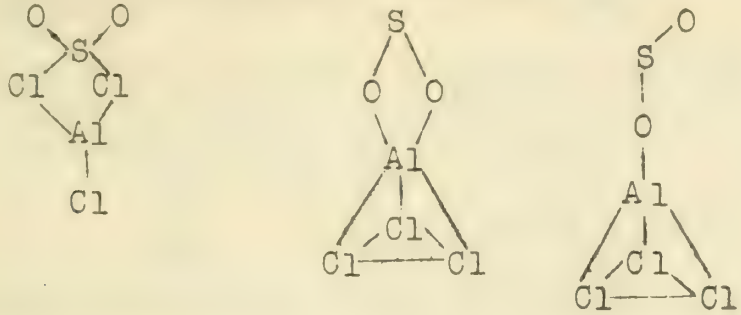


which being negatively charged would then combine with IV to form:

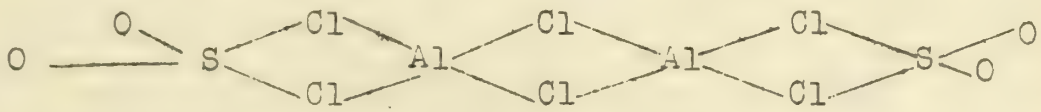


Since no 2:1 addition compound, $2SO_2$-BF_3, has been noted to date this might be used as evidence that liquid sulfur dioxide dissociates as Wickert has pointed out.

The system $AlCl_3$-SO_3 has been studied by various investigators who have indicated that a 1:1 addition compound is formed. Gerding and Smit (12) prepared the compound and proposed three structural formulas:

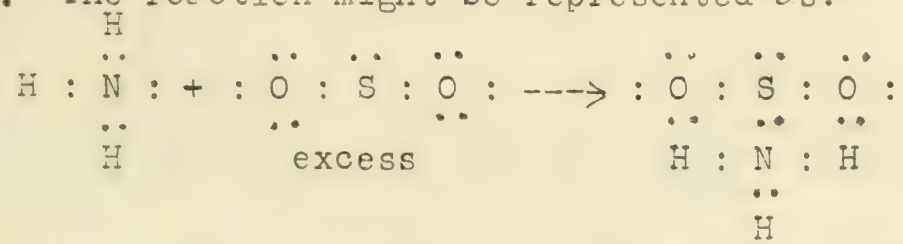


but experimental evidence seems to be best in agreement with a double molecule, Al_2Cl_6-$2SO_2$,

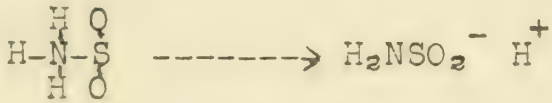


Ammonia (1) and various nitrogen containing compounds (2) form complexes with sulfur dioxide. Ephraim and Piotrowski (1) have shown that three different compounds are formed by the interaction of sulfur dioxide with ammonia, depending on the conditions and relative amounts of reactants.

With an excess of sulfur dioxide, a compound SO_2-NH_3, which may be represented as amidosulfinic acid, NH_2SO_2H, is always formed. The reaction might be represented as:



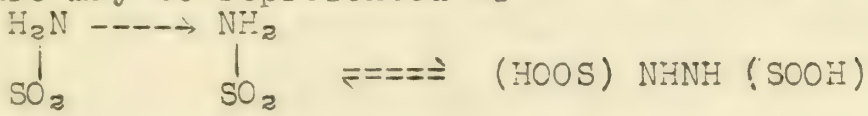
and it may be assumed that the sulfur atom acts as an acceptor and the nitrogen atom as a donor, followed by rearrangement of the addition compound to the amido sulfinic acid by simple proton migration:



With an excess of ammonia two products are formed, one a white compound with the composition SO_2-$2NH_3$ and the other a red compound with the same percentage composition but double molecular weight, $2SO_2$-$4NH_3$. The white product has been shown to be ammonium amido sulfite, $NH_2SO_2NH_4$, and the red compound triammonium imidosulfinate, NH_4-$N:(SO_2$-$NH_4)_2$. That one of the nitrogens of the red compound has a different link than the other three is shown by the preparation of a silver salt, $AgN:(SO_3Ag)_2$, which is also red in color, such colored salts often being obtained when metals are directly combined with nitrogen.

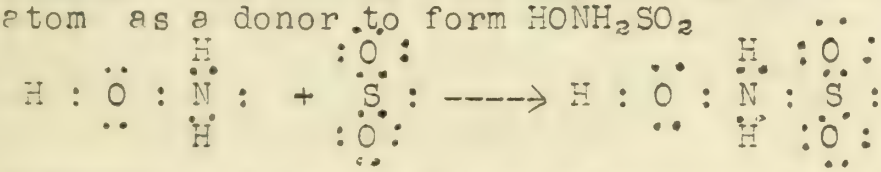
When amidosulfinic acid is heated under dry carbon disulfide in a reflux apparatus, decomposition with the evolution of ammonia is noticed, and a dark red crystalline sublimate of the composition $3SO_2$-$4NH_3$ is obtained.

When sulfur dioxide is passed into an anhydrous alcholic solution of hydrazine, a white, crystalline precipitate is formed whose structure may be represented as

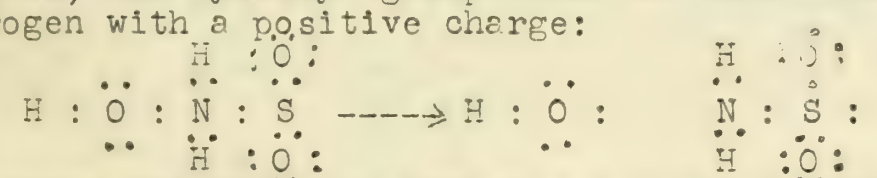


Here again the sulfur atoms are electron pair acceptors.

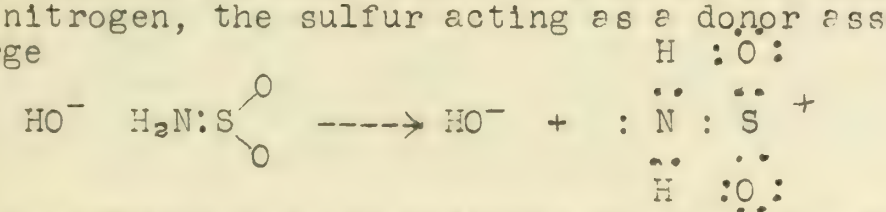
Hydroxylamine reacts with sulfur dioxide to form sulfamic acid. $NH_2OH + SO_2 \xrightarrow{H_2O} NH_2SO_3H$
Sisler and Audrieth (9) have shown that the yields are better and the reaction time shorter if the reaction is carried out under pressure. The mechanism of the reaction is essentially as follows: The sulfur atom may act as an acceptor, the nitrogen atom as a donor to form $HONH_2SO_2$



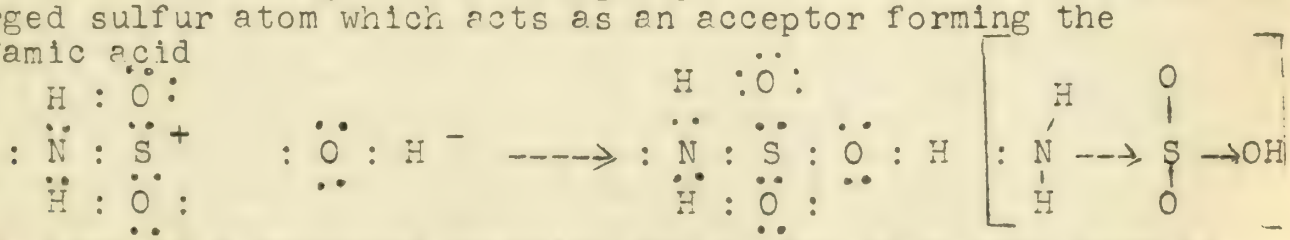
The $HONH_2SO_2$ may then undergo a Beckmann type rearrangement; that is, the hydroxyl group forms an ionic bond leaving the nitrogen with a positive charge:



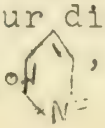
but since the nitrogen atom has a greater affinity for electrons than sulfur, the free electron pair on the sulfur may shift to the nitrogen, the sulfur acting as a donor assuming a positive charge

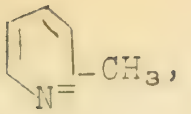


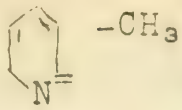
The negatively charged hydroxyl group unites with the possitively charged sulfur atom which acts as an acceptor forming the sulfamic acid



Thus, here is a compound in which the sulfur atom acts both as a donor and as an acceptor.

Various organic compounds containing nitrogen form coordination compounds with sulfur dioxide. Hoffman and Werf (20) in 1946 showed that pyridine,  , forms a single stable compound, SO_2-C_6H_5N, m.p. -7.4°

alpha picoline,  , forms two stable compounds with SO_2
1. $3SO_2 2CH_3C_5H_4N$, melts at -17.8°
2. $SO_2-CH_3C_5H_4N$, melts at -19.4°

beta picoline,  , forms one stable compound $SO_2-CH_3C_5H_4N$, melts at -15.0°

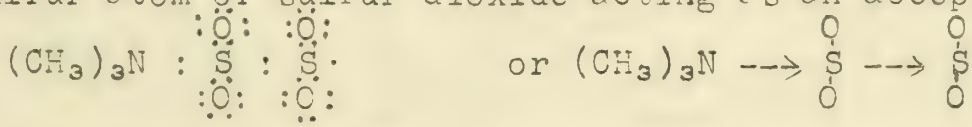
gamma picoline,  , forms two compounds with sulfur dioxide
1. $SO_2-CH_3C_5H_4N$, melts at 5°
2. $2SO_2-CH_3C_5H_4N$, undergoes transition at its melting point at -26.5°. This may be the result of the 1:1 compound undergoing solvation.

Unlike most addition compounds, those resulting from the addition of sulfur dioxide to pyridine and picolines gives colorless compounds. Burg (17) presents evidence that trimethyl amine and sulfur dioxide form a 1:1 addition compound simply by electron sharing between the nitrogen and sulfur atoms - the sulfur atom acting as an acceptor.

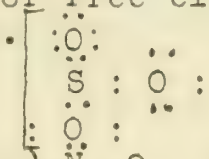
$$(CH_3)_3N: + SO_2 \longrightarrow (CH_3)_3N \rightarrow SO_2$$

He offered evidence that it does not exist as an ionic dimer $[(CH_3)_3N]_2\ SO^{++}SO_3^{--}$. Jander and Wickert (7) advocated the formula $[(C_2H_5)_3N]_2\ SO^{++}\ SO_3^{--}$, for the addition product of sulfur dioxide and triethylamine.

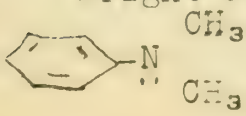
Burg points out that the 1:1 addition compound of trimethylamine is soluble and is apparently solvated in liquid sulfur dioxide; this could be due to a possible tendency for the sulfur atom of the trimethylamine addition compound to act as a donor with the sulfur atom of sulfur dioxide acting as an acceptor.



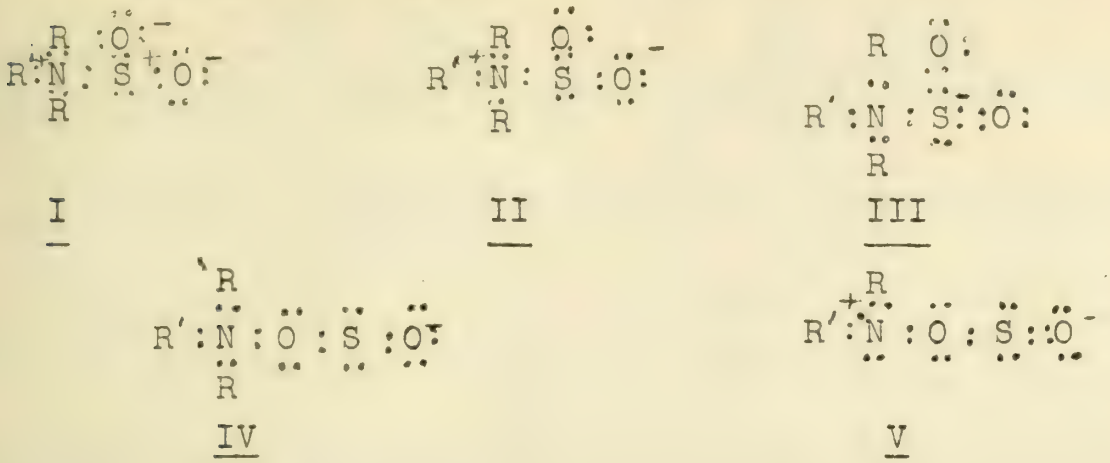
It is interesting to note that trimethylamine forms a 1:1 addition compound with sulfur trioxide; this 1:1 addition compound has much less solubility in sulfur dioxide than $(CH_3)_3NSO_2$, probably indicating the lack of free electron pairs on the sulfur atom of sulfur trioxide.



Trimethylamine oxide, $(CH_3)_3N\rightarrow O$, reacts with sulfur dioxide at low temperatures to yield the 1:1 addition compound, $(CH_3)_3NOSO_2$, indicating that the amine oxide as the hydroxyl ion $(OH)^-$ has strong electron donor properties. This 1:1 addition compound adds another molecule of sulfur dioxide; it is not known whether the free electron pair of the sulfur acts as a donor or if a free electron pair on the oxygen atom of the amine oxide acts as the donor. However, Burg indicated that the order of decreasing attraction for sulfur dioxide appears to be $(CH_3)_3NO > (CH_3)_3N > (CH_3)_3NOSO_2 > (CH_3)_3NSO_2 > (CH_3)_3NSO_3$

Bright and Fernelius (15) have shown that dimethylaniline,  , forms an addition compound with sulfur dioxide.

Unlike Burg. they propose a N-O-S linkage instead of a N-S-O linkage. They propose 5 possible structures: ($R' = C_6H_5$; $R = CH_3$)



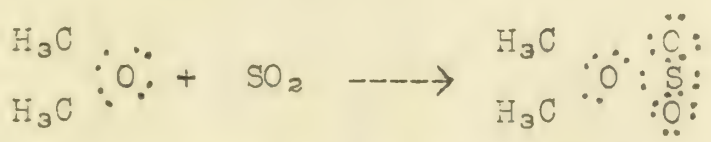
I II III

IV V

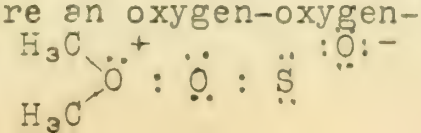
From experimental data the parachor of the addition compound measures 405.4, which is within 2% of 396.8, the value obtained from the sum of the atomic and structural parachors for structures I and IV. However, Bright and Fernelius state that structure I is unlikely because of adjacent positive charges, and II, III, and V are unlikely because the sulfur atom has more than an octet and because the double bonds makes the sum of the additive parachors too high over the value obtained from experimental results. Thus, they conclude that structure IV seems the most probable. Although not stated in their article, if this is true, then the oxygen atom is acting as an acceptor for the free pair of electrons from the nitrogen.

Bright and Jasper (16) for similar reasons assigned the structural formula $(C_2H_5)_3N^+ : \ddot{O} : \ddot{S} : \ddot{O}^-$ for the 1:1 addition product of triethyamine with sulfur dioxide, and the structure $(C_3H_7)_3N^+ : \ddot{O} : \ddot{S} : \ddot{O}^-$ for the addition compound with tripropylamine. (19)

Albertson and Fernelius (18) point out that various oxygen containing compounds form addition compounds with sulfur dioxide. They believe the 1:1 addition compound between sulfur dioxide and dimethyl ether is best explained by assuming that the ether oxygen atom shares a pair of its electrons with the sulfur atom of sulfur dioxide:



If this is true note the adjacent positive charges in the sense that Bright and Fernelius assigned them in case of formula I above. Thus it seems that either the existence of a N-S-O link in R_3N-SO_2 compounds cannot be ruled out as unlikely because of adjacent like charges, or that a different type of linkage exists between the oxygen atom of dimethyl ether and sulfur dioxide than is explained above; to be similar to that proposed by Bright and Fernelius in case of tertiary amines, would require an oxygen-oxygen-sulfur link,

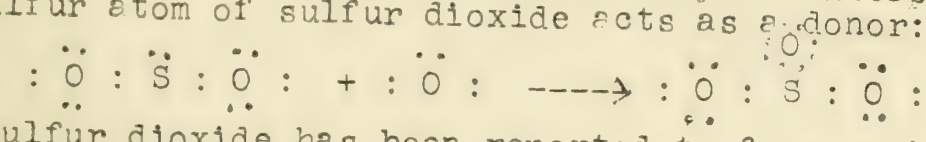


It is interesting to note no reference has been found in which Fernelius measured the parachors of such oxygen containing compounds as dimethyl ether -- sulfur dioxide, but has proposed that the oxygen atoms of anesole, dioxane, acetone donate electrons to sulfur atoms of sulfur dioxide.

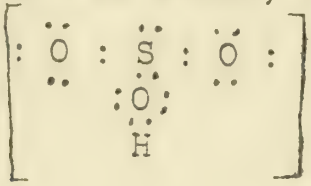
Diethyl sulfide forms an addition compound similar to that of hydrogen sulfide:

Note here also the existence of adjacent positive charges. To have a structure similar to the N-O-S link proposed for the addition compounds of tertiary amines and sulfur dioxide would require a S-O-S linkage:

The work of Hagg (5) in regard to the ease of oxidation of sulfur dioxide to sulfur trioxide may be interpreted to mean the sulfur atom of sulfur dioxide acts as a donor:

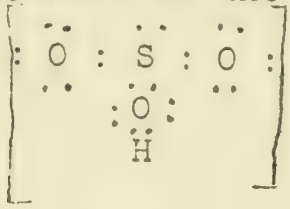


Sulfur dioxide has been reported to form various hydrates; most evidence is in favor of SO_2-$6H_2O$. It is probable that the sulfur atom acts as an acceptor for a free electron pair from one molecule of water, or of a hydroxyl ion, forming



H_3O^+; the balance being associated through hydrogen bonding.

Since sulfurous acid ionizes $H_2SO_3 \overset{H_2O}{\rightleftharpoons} H_3O^+ + HSO_3^-$ it may be a hydrate of the type:



H_3O^+

1. Ephraim and Piotrowski, Ber. 44, 379 (1911)
2. ibid. 44, 386 (1911)
3. Silberhead, Proc. Chem. Soc. 121, 1015 (1922)
4. Germann and Booth, J. Phys. Chem. 30, 369 (1926)
5. Hagg, Z. physik. Chem. B18, 199 (1932)
6. Hill and Fitzgerald, J. Am. Chem. Soc. 57, 250 (1935)
7. Jander and Wickert, Ber. 70B, 251 (1937)
8. Wickert, Z. Electrochem. 44, 410 (1938)
9. Sisler and Audrieth, J. Am. Chem. Soc. 61, 3389 (1939)
10. Bright and Jasper, ibid. 63, 3486 (1941)
11. Gur'yanova, Physicochem (U.S.S.R.) 16, 181 (1942)
12. Gerding and Smit, Z. Physik. Chem. B51, 200 (1942)
13. Booth and Martin, J. Am. Chem. Soc. 64, 2198 (1942)
14. Fischer and Burger, Z. Anorg. Algem. Chem. 251, 355 (1943)
15. Bright and Fernelius, J. Am. Chem. Soc. 65, 637 (1943)
16. Bright and Jasper, ibid. 65, 1262 (1943)
17. Burg. ibid. 65, 1629 (1943)
18. Albertson and Fernelius, ibid. 65, 1687 (1943)
19. Bright and Jasper, ibid. 66, 105 (1944)
20. Hoffmann and Werf, ibid. 68, 997 (1946)

THEORIES CONCERNING THE PASSIVITY OF METALS

April 22, 1947 Peter G. Arvan

The phenomenon of passivity of metals was discovered by Keir (1) in the year 1790. He observed that iron, after treatment with concentrated nitric acid, lost the property of precipitating silver from solutions of silver salts, and was no longer attacked by dilute nitric acid. The name passivity is due to Schönbein (2), who made many important contributions to the knowledge of the subject. Faraday's (3) name is also closely associated with the early history of the phenomenon.

For a number of years after 1840, little progress was made in this field, but about 1900 a new era of advance set in. This stage was initiated by the experimental investigations of Hittorf (8), who worked chiefly with chromium. Other investigators of this time are Le Blanc (9, 17), Foerster (15), Haber (4, 5), Müller (7, 11), Schmidt (16), and Krassa (6). Since 1918 the predominating names have been U. R. Evans (19), Tronstad, W. Hughes, and E. S. Hedges (20).

The Theories of the Passivity of Metals

1. The oxide film theory (3, 4, 5, 6, 7, 20)
   The mode of action of a film of oxide or other insoluble substance in causing passivity is presumably that it coats the electrode and mechanically hinders metallic ions from entering the solution. Current can only pass when the anode potential is increased to such an extent that anions are discharged. This theory was proposed by Farady (3), generally accepted until about 1900, and then abandoned only to be revived in 1926 by U. R. Evans (19).

2. The valence theory of passivity (10)
   This theory, first brought forth by Finkelstein (10), is based on the assumption that the modifications of a metal with different valencies are all present in the solid metal, in proportions depending on temperature and other factors, and that the electrochemical behavior of metals depends on the relative concentration of these modifications.

   The main point of the valence theory is that the cause of passivity is to be sought in the metals themselves. This theory met with very little support and has been almost discarded.

3. The reaction-velocity theory (9)
   This theory was proposed by Le Blanc and in its most general form states that passivity phenomena are due to slow rate of change (electrochemical or purely chemical) at the anode. This theory is little more than the statement of the facts, and several special hypotheses have been put forward as regards the mechanism of retardation of the reactions at the anode.
   (a) The oxygen charge hypothesis (12, 13)
   The cause of passivity is to be sought in the slow rate of reaction between the anode and the oxygen liberated, with the result that the anode becomes

charged with gas, or, alternately, a metal-oxygen alloy is formed. The sudden changes from the active to the passive condition are ascribed to the transition from a non-homogeneous state of polarization into a continuous gas charge covering the electrode uniformly.

(b) The anion discharge hypothesis (14)
According to this hypothesis, the main change at the anode is not the formation of metal ions but the discharge of anions; the slow reaction of the discharged anions with the metal produces passivity.

(c) The hydrogen activation hypothesis (15, 16)
This theory is based on the assumption that the pure metal is passive and becomes active only under the influence of a catalyst.

(d) The retarded ion hypothesis (17)
In this theory the assumption is made that the active metal sends out ions into the electrolyte, and that in the case of metals which tend to become passive, these ions combine only very slowly with water.

Ion + water ⇄ ion hydrate

Bibliography

"Transactions of the Faraday Society," 9, 203 (1914)

McKay and Worthington, Corrosion Resistance of Metals and Alloys, Reinhold Publishing Corporation, New York, (1936)

Evans, U. R., The Corrosion of Metals, Arnold and Co., London, (1924)

1. Keir, Phil. Trans., 80, 359 (1790)
2. Schönbein, Pogg. Ann., 37, 390 (1836); 43, 103 (1938)
3. Faraday, Phil. Mag., 9, 53 (1836)
4. Haber and Goldschmidt, Zeitsch. Electrochem., 12, 49 (1906)
5. Haber and Maitland--ibid; 13, 309 (1907)
6. Krassa, Zeitsch. Electrochem., 15, 490 (1909)
7. Müller and Spitzer, Zeitsch. anorg. chem., 50, 321 (1906)
8. Hittorf, Zeitsch. physikal. Chem., 25, 729 (1898); 30, 48, (1899); 34, 385 (1900)
9. Le Blanc, Zeitsch. Electrochem., 6, 472 (1900); 11, 9 (1905)
0. Krüger and Finkelstein, Zeitsch. physikal. Chem., 39, 104 (1902)
1. Müller, Zeitsch. physikal. Chem., 48, 577 (1904)
2. Fredenhagen, Zeitsch. physikal. Chem., 43, 1 (1903); 63, 1 (1908)
3. Muthmann and Frauenberger, Sitzungsber. der Kgl. Bayrischen Akad., 34, 201 (1904)
4. Sackur, Zeitsch. Electrochem., 14, 612 (1908)
5. Foerster, Abhandlungen der Bunsen Gesellschaft, 1909, No. 2
6. Schmidt, Zeitsch. physikal. Chem., 77, 513 (1911)
7. Le Blanc, Lehrbuch der Electrochemie, 5th edition, p. 285
8. Russell, Nature, 115, 455 (1925)
9. Evans, Nature, 118, 51 (1926)
0. Hedges, Chem. and Ind., 50, 750--1 (1931); 1219 (1927)

ZIRCONIUM

Roy D. Johnson April 29, 1947

I. General (1,2,3,4,5,6)

Zirconium is rapidly emerging from its obscure position as "one of the less familiar elements" through greatly expanded commerical interest and usage. In spite of the fact that zirconium is one of the twenty most abundant elements and is more plentiful than nickel, tin, copper, lead, and zinc combined, its use up to 1892 was severely hampered by the stability of $ZrSiO_4$, its chief ore. The discovery of baddelyte, a zirconium oxide ore, in nature has made zirconium and its compounds much more readily available.

II. History (1,2)

Klaproth in 1789 found a new earth which he called "Zirconia" in analyzing the precious stone from Ceylon known as jargon. Berzelius (1824) was the first to obtain the element zirconium in impure form. He obtained amorphous zirconium by reducing K_2ZrF_6 with potassium. This method is still one of the best for reducing zirconium to the elemental stage. After many false 'discoveries' of new elements in zirconium ores had been reported, the element hafnium was found in zirconium ores by Coster and v. Hevesey in 1923. Since hafnium is very similar to zirconium, no attempt to separate the two is made in industry.

III. Zirconium-the element

Elemental zirconium has been prepared as a fine black or dark gray powder and as the lusterous ductile metal.

Zirconium powder (2,6,7) is generally prepared from the purified oxide by a thermit reaction with Na, Mg, Al, or Ca, and purified by special methods. While the powder is stable and relatively inert at ordinary temperatures, it ignities in air when heated to 210-275°C. The heat of combustion is approximately 1956 calories/gram. These properties make it valuable in primer mixtures as it doesn't deteriorate, react with the other components, or form an amlgam with mercury on standing. Above 200° the powder is an excellent getter. When it is used in vacuum tubes for this purpose, the powder is mixed with a binder and sprayed on the anode assembly. The good black surface obtained by this method allows the use of smaller plates by reason of its high heat of radiation. The powder has been pressed into bars, sheets and wire, but these in general have been brittle and unsatisfactory. Zirconium powder has also been used in blasting caps, pyrotechnics, tracer ammunition, and X-ray tube filters.

Ductile zirconium (2,6,9,10,11) is prepared by the method of de Boer. Somewhat impure zirconium powder is placed in a pyrex container with a little iodine. After the vessel is evacuated, it is heated gently to about 400° thus vaporizing the iodine and forming ZrI_4. A hairpin tungsten filament is then heated to about 1300°, and very pure crystalline zirconium deposits on the filament with the liberation of the iodine. The powder used must be free of other elements having volatile iodides (e.g. Ti, Sn) as the iodine carrier action would cause

them to codeposit and greatly decrease the ductility of the product. When deposited at 1300°, zirconium crystallizes in a body centered cubic lattice (beta-Zr) while at room temperature it has a closely packed hexagonal lattice (alpha-Zr). On cooling, the transformation takes place at 865°. The external form, however, remains beta thus giving an interesting example of pseudo morphism.

Ductile zirconium possesses a white metallic luster which does not tarnish on long standing. It is attacked by concentrated sulfuric acid at 100°C. or by HF, but not by 50% H_2SO_4 at 100°, any concentration of HCl or HNO_3, aqua regia at room temperature, 10% NaOH at 100°, 50% NaOH at 100°, or H_2S.

The use of zirconium as a getter depends on its great affinity for oxygen, nitrogen, carbon monoxide, carbon dioxide, hydrogen and water vapor. It absorbs none of the rare gases. Definite compounds possessing crystalline forms different from zirconium are formed with oxygen, nitrogen, and hydrogen (ZrO_2, ZrN, and ZrH_2). When one starts with the pure metal, it seems that large amounts of these three gases can be absorbed without the formation of a new phase. Absorption of hydrogen is reversible but that of oxygen and nitrogen is not. Oxygen is absorbed above 700° and nitrogen above 1000°. Hydrogen is absorbed fairly readily at 300° and more rapidly at 1000°, but at 1500° ZrH_2 is completely decomposed.

Formation of the oxide raises the melting point, electric resistivity, and atomic distance but decreases ductility. The behavior of nitrogen is similar except for the fact that the nitride is a better conductor than the metal itself. Zirconium rendered brittle by hydrogen becomes ductile again on heating to a high temperature in vacuo.

When zirconium wire is used as a getter in vacuum tubes (11), it is usually wound around a core, since the zirconium alone is relatively weak. A companion wire serves to prevent creepage and the formation of liquid zirconium globules around the core. Ductile zirconium is also used as a getter for metal evaporation on ceramics, glass and metals; as a welding flux, grid emission inhibitor, and vacuum accelerator; and for rayon spinnerets, sutures, surgical repair plates, and ceramics and glass decoration.

IV. Zirconium alloys (6)

Interest in zirconium alloys arose chiefly from its use in the steel industry as a scavenger where the addition of 0.15% zirconium is reported to markedly decrease nometallic inclusions and to counteract the effects of a high sulfur content - ZrS_2 in steel does not cause brittleness.

Zirconium alloys with many metals including Si, Al, Ti, Mn, Fe, Cu, and Ni. The solubility of zirconium in these metals seems to be very small. As the amount of zirconium is increased beyond a few tenths of a percent, definite compounds are formed. Approximate formulas for some of these compounds are as follows: Al_4Zr_3, (Fe_3Zr_2 or Fe_2Zr), Cu_3Zr, Ni_3Zr and Ni_4Zr. An uninterrupted series of solid solutions is obtained with hafnium. Perhaps the most interesting alloy from the industrial viewpoint is one of copper, containing 0.1 - 5% zirconium. The electrical conductivity of the copper remains essentially unchanged, while the tensile strength and hardness are increased up to 50%. The alloy will not soften up to 450° and is suitable for use in electric leads and in spot welding electrodes.

V. Zirconium compounds (1)

Zirconium forms three general types of compounds, the normal salts, Zr^{+4}; zirconyl salts, ZrO^{+2}; and zirconates, ZrO_3^{-2}. Of these, the zirconyl compounds are far in the majority as the normal salts are generally stable only in strong acids while strong bases are required to obtain zirconates.

$ZrSiO_4$ (4, 12, 13) is the most abundant zirconium compound. Zircon's melting point of 2550° is quite high, and, in addition, it is extremely inert being insoluble in all acids except hydrofluoric. These properties coupled with the low coefficient of thermal expansion of zircon, lead to its chief uses in special porcelains and refractories. Zircon-silica glass is less sensitive to temperature change and more resistant to acids and alkalies than ordinary glass. Zircon also finds some use in enamels, cements, in the preparation of zirconium alloys, and as an inert white pigment. Artificial zircons as well as the natural stones are now available commercially. It has been reported that a mixture of ZrO_2 and silica heated to 1460° is converted to a zirconium silicate identical with the mineral.

Zirconia (3, 14) is perhaps the most important zirconium compound commerically because of its large use as an opacifier in enamels. It is a white talc like powder which melts at 2950±20° and is a good insulator for heat and electricity. Its stability is indicated by the high heat of formation (264K calories/mol). The coefficient of expansion of 8×10^{-7} is slightly higher than that of silica. Three crystalline forms have been reported. The monoclinic form, which is precipitated under ordinary conditions, changes over to the tetragonal with a marked shrinkage in volume on heating over 1000°. This change is reversible on rapid cooling. It is reported that a trigonal or pseudo hexagonal rhombic form is obtained when ZrO_2 is fired above 1900° for long periods. Some workers believe that this is the stable crystalline form although it has not been found in nature. Taking these facts into account, there are two methods for making satisfactory zirconia refractories: A. by preparing the "stable" trigonal form, and B. by adding 4 to 40 mol percent of magnesium oxide to the zirconia and heating above 1700°. In this region the two oxides form a series of solid solutions giving a stable homogeneous cubic phase. Refractories made in the latter manner are unusable above 2000°. Zirconia is also used as a paint pigment, in glass, for safe and vault walls, and as a catalyst in the preparation of gasoline from olefins.

Zirconium hydroxide (2) is obtained by precipitating a salt solution with caustic soda or ammonia. It comes down as a bulky gelatinous mass which retains a great deal of water. The anhydrous compound may be obtained by drying in vacuo over sulfuric acid. Zirconyl hydroxide, $ZrO(OH)_2$, is obtained at 100° or by precipitation from boiling solution. Zirconyl hydroxide is amphoteric as it forms zirconyl salts in the presence of mineral acids and zirconates on fusing with a suitable alkalies. Organic alpha hydroxy acids give soluble complex compounds with zirconium in alkaline solution. Thus, when tartaric acid is present, zirconium is not precipitated by caustic soda. Only when the solution is exactly neutralized does the hydroxide come down. The same effect is obtained with 1,2 dihydroxy alcohols and 1,2 aromatic phenols.

Zirconium sulfate (1,2) is prepared by the following reaction: ZrO_2 + conc. H_2SO_4 $\xrightarrow{>400^\circ}$ $Zr(SO_4)_2$
It is useful in the detection of potassium as Na^+, NH_4^+, Cs^+, Rb^+, Li^+, and Mg^{++} do not interfere. The normal sulfate reacts with water to give $ZrOSO_4$. The zirconyl sulfate finds considerable use as a tanning agent (15,16,17) for the best white leather. Leather tanned with this agent is white all the way through, stable, washable, unaffected by shoe cleaners, resistant to hot water, and absolutely fast to light. A wide range of basicity has been found permissable in the tanning process, making it easy to control under practical conditions. It can also be used with chrome for tanning as a substitute for part of the chrome or as a retan on chrome tanned leather to give additional weight.

Zirconium carbide, ZrC, (1,18) is of interest because of its extremely high melting point, 3532°C. It reacts to a small extent with dilute nitric acid but immediately and violently with concentrated nitric acid or aqua regia. Caustic potash dissolves it readily. The carbide finds some use in cutting tools because of its low heat conductivity, hardness, and refractory nature. When the oxide is reduced with an insufficient amount of carbon, a mixture of ZrC and ZrO_2 suitable for use as an abrasive is obtained.

Zirconium halides (1,2,4) are quite similar so the discussion here will be confined primarily to the chlorides. The normal chloride sublimes at about 350°. On cooling the vapor, the chloride condenses to well shaped white needles which fume in air with hydrolysis to $ZrOCl_2$. Zirconyl chloride crystallizes in well shaped colorless needles with eight molecules of water of hydration. It cannot be completely dehydrated without decomposition.

Some facts of interest on other zirconium compounds (19) are given in the following table.

VI. Bibliography

1. F. P. Venable, "Zirconium and its Compounds," Chemical Catalog Co., N.Y., N.Y. (1922).
2. J. H. deBoer, Foote Prints, 3, No. 2, 1 (1930).
3. J. D. Fast, Foote Prints, 10, No. 2, 1 (1937).
4. B. S. Hopkins, "Chapters in the Chemistry of the Less Familiar Elements, "Chap. 12, Stipes Pub. Co., Champaign, Ill. (1939).
5. A. E. van Arkel, "Reine Metalle, "191, Edwards Brothers, Ann Arbor, Mich. (1943).
6. W. M. Raynor, Foote Prints, 15, No. 2, 3 (1943).
7. G. H. Chambers, Metals and Alloys, 4, No. 12, 199 (1933).
8. US Pat. 1760 413 (1930).
9. H. W. Gillett, Foote Prints, 13, No. 1, 1 (1940).
10. J. D. Fast, Foote Prints, 13, No. 1, 22 (1940).
11. G. A. Eperson, Foote Prints, 18, No. 1, 3 (1946).
12. H. C. Meyer, Foote Prints, 9, No. 1, 1 (1936).
13. G. C. Betz, Foote Prints, 9, No. 2, 15 (1936).
14. E. Preston, Foote Prints, 11, No. 2, 1 (1938).
15. I. C. Sommerville, J. Am. Leather Chem. Assoc. 36, No. 8, 381, (1942).
16. H. G. Turley and I. C. Somerville, J. Am. Leather Chem. Assoc. 36, No. 8, 391 (1942).
17. I. C. Somerville and H. G. Turley, J. Am. Leather Chem. Assoc., 38, No. 9, 326 (1943).
18. Agte and Alterthum, Zeit. tech. Physik, 11, 182 (1930).
19. Rahm and Haas advertizing literature.

Compound	Formula	Interesting Properties	Possible Uses
Zirconyl nitrate	$ZRO(NO_3)_2.3H_2O$	Cream powder, Dry liberates NO slowly conc. solutions stable	Prep. mixed oxide catalyst, food preservative
Ammonnium Ziirconyl Tartrate	*$(NH_4)_2(ZrO)_2$ $tart_3),5H_2O$	Light tan crystalline, very soluble H_2O stable in alkali to pH10, hydroscopic	Mordanting and dyeing leather, protein precipitant
Potassium Zirconyl Oxalate	*$K_2H_2(ZrO(C_2O_4)_3\cdot$ $4H_2O$	White crystalline, water soluble, pH of solution lowers slightly on heating stable solution, 59.30°C pH = 3	Mordanting and dyeing leather, acid fixing baths
Potassium Fluo-Zirconate	K_2ZrF_6	White crystalline, neither solid or solution attacks glass, molten salt is stable alkali precipitates ZrO_2, H_3PO_4 no effect	Facing compound light alloy molds.
Zirconyl stearate	$ZrO(C_{18}H_{35}O_2)_2$	Light tan lakes, soluble organic solvents, inorganic soap, m.p. 60°, decomposed by strong acids and alkali	Water repellents, grease and oil addatives, high temperature lubricant
Zirconyl acetate	$ZrO(C_2H_3O_2)_2$	Light reddish brown liquid, pH = 4.5, hydrolysis gives a gel.	Source soluble Zirconium, weighting filler for silk
Zirconyl formate	$ZrO(CHO_2)_2.2HCO_2H$	Light brown liquid, pH = 3, immiscible organic solvents, miscible H_2O, can be boiled without hydrolysis	water repellent
Hydrated Zirconium (Tech)	$ZrO_2.XH_2O$	White semisolid gel-unignited reactive calcined gives porous oxide	Catalyst, source soluble Zr (95-97% of ZrO_2 soluble in mineral acids)
Zirconyl phosphate	*$5ZrO_2.4P_2O_5.$ $19H_2O$	White powder, very insoluble, alkali fusion required to decompose salt which has been ignited to 850°C.	Refractory manufacture special glasses, catalyst for cracking hydrocarbons

* Approximate formula